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Supercritical Fluid Regeneration of Activated Carbon Used for Volatile-Organic-Compound Vapor Adsorption

Arthur D. Little, Inc.
Cambridge, MA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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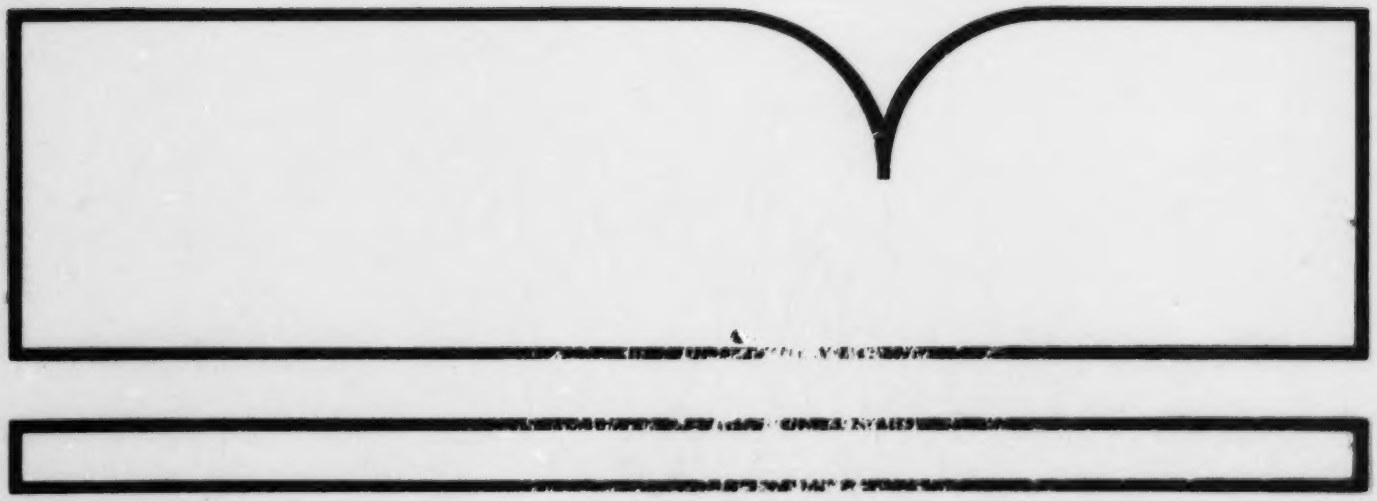

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SUPERCRITICAL FLUID REGENERATION OF ACTIVATED CARBON USED FOR VOLATILE-ORGANIC-COMPOUND VAPOR ADSORPTION

by

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ABSTRACT

The objective of this program was to develop a sound fundamental technical base for supercritical-fluid regeneration of activated carbon applied to adsorption of volatile organic compounds. The process is based on using a supercritical fluid for desorbing granular activated carbon containing adsorbed vapor contaminants. The desorption is carried out at high pressure, and is followed by a distillation of the fluid-adsorbate mixture at subcritical conditions for removal of contaminants and recovery of fluid solvent for recycle. The two key unit operations characterized were (1) desorption from the carbon bed, and (2) distillation of the solvent-adsorbate solution.

The process was characterized for both leaded and unleaded gasoline vapors, representative of contaminants from gasoline storage and distribution facilities; and for ethanol and methyl ethyl ketone vapors, representative of numerous solvent finishing operations.

Commercial vapor-phase activated carbon loaded with gasoline vapor components, ethanol or MEK vapor could be completely regenerated with supercritical CO_2 at 1500 psia and 50°C. A carbon adsorption/supercritical CO_2 regeneration system to purify 10,000 SCFM of air containing one-quarter of the lower explosive limit of MEK was estimated to have a price of $530,000 (December, 1980), a yearly operating cost of $285,000, and an MEK recovery value (pure MEK is recovered) of $1,386,000, or a payout period of less than one year.

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I. INTRODUCTION

Activated carbon has been shown to be effective for atmosphere contamination control because of its ability to adsorb a wide range of organic compounds. The principal drawback of existing processes using carbon for the control of organic vapor emissions has been the requirement for a large carbon inventory to compensate for the inability of the regeneration technique to keep the carbon working capacity from declining over the course of multiple adsorption/regeneration cycles. However, process studies at Arthur D. Little have shown that supercritical fluids (fluids in the region above their critical temperatures and pressures) can rapidly and effectively regenerate activated carbon loaded with a broad range of organic compounds. The use of this regeneration method could favorably influence the economics of carbon used in emission control.

The essential features of the supercritical fluid process are set forth in a simplified process flowsheet, Figure I.1. In the adsorption cycle, air contaminated with organic vapor is flowed through the granular activated carbon bed until breakthrough. Loaded carbon is then transferred to the pressure desorption vessel, and the desorption cycle is then begun. Supercritical fluid at conditions which favor the desorption of the component adsorbed on the carbon is flowed through the carbon bed. The effluent regenerant stream is rendered subcritical by alterations of its pressure and/or temperature, and a vapor-liquid separation (distillation) of this stream is effected to recover the solvent fluid for recycle. The regeneration system is efficient because the supercritical fluid has high solubility for the carbon adsorbates, favorable mass transfer properties for rapid desorption, and high volatility for subsequent separation of solutes. Carbon dioxide is particularly suitable as the solvent; its critical temperature and pressure (31.0°C and 72.8 atm) are economically attainable, it has high solubilities for organic compounds, it is fairly dense at process conditions (therefore power requirements for compression are reasonable), and it is non-flammable and non-toxic.

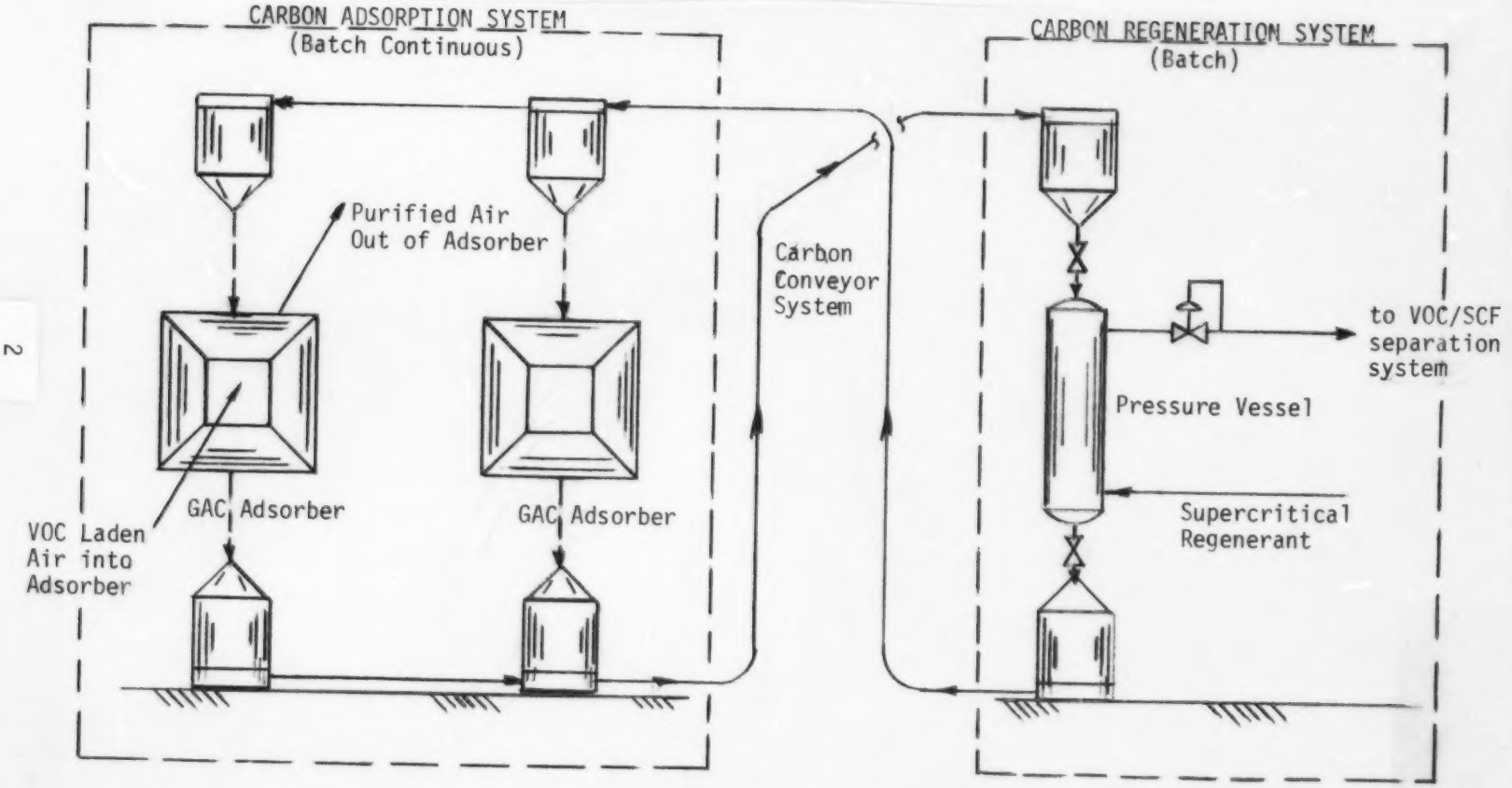

Figure I.1
Simplified Process Flow Sheet for Supercritical-Fluid
Regeneration of GAC Used for VOC Adsorption

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Where desirable, adsorbate can be recovered in reasonably pure form without a requirement for a water-adsorbate separation process.

The objective of this program was to develop process information and economic estimates for this emission control system. The two key unit operations characterized were:

(1) the desorption of the carbon bed with the supercritical fluid, and
(2) distillation of the solvent-adsorbate mixture.

The program involved combination of an analytical and experimental approach to obtain proper characterization of parameters for the design of each unit operation. Specifically, the desorption operation was characterized for four test adsorbates. Two of these were volatile organic compounds (VOC's) representing important industrial solvents: ethanol and methyl ethyl ketone. The two other adsorbates were vapors from leaded and unleaded gasoline. For each of these, a range of regeneration conditions was evaluated using carbon dioxide as the regenerating solvent.

The process analysis and design phase included evaluation and selection of CO_2/adsorbate separation processes. Efficiency, low-cost, and component purities were criteria used in the evaluation.

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II. CONCLUSIONS

1. Essentially complete regeneration of commercial vapor-phase granular activated carbon loaded with gasoline vapors is achievable using supercritical or near-critical carbon dioxide and Freon-13. Best results were obtained with supercritical CO_2; liquid CO_2 and liquid Freon 13 were slightly less effective, in terms of quantity of residuals left on the carbon after regeneration. Depending on process conditions, residuals of 0-10% of virgin capacity were seen.

2. Toluene, which has been observed as a principal component of gasoline vapor heel on carbon, can be removed completely from carbon using CO_2 and Freon-13 at critical conditions.

3. Gas-phase CO_2 at 35 atm (500 psia) is ineffective in regenerating carbon loaded with toluene.

4. Leaded and no-lead gasoline give the same regeneration behavior.

5. For regeneration of carbon loaded with gasoline vapors, little effect of CO_2 pressure was seen in the range of 100-200 atm. Improved regenerability was seen at 50°C vs 25°C.

6. Carbon loaded with ethanol and methyl ethyl ketone vapors was regenerated with CO_2 at 25°C and 100 atm, leaving no residual.

7. A seventy-five cycle test was run, with negligible residual detectable at its conclusion. The adsorption cycles included 25 each for leaded gasoline, ethanol, and methyl ethyl ketone vapors.

8. Calculated results showed that CO_2 purification for recycle and adsorbate recovery could be achieved by distillation. CO_2-n-butane cases were run to simulate the CO_2-gasoline vapor separation; CO_2-MEK was run as a VOC worst case. High-purity CO_2 can be produced, adsorbate recovered with small CO_2 losses, and distillation can be run with good energy economy.

9. Process cost estimates indicate that carbon loaded with MEK can be regenerated for about 2¢/lb. Capital cost for a 10,000 CFM system is

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$530,000, which is higher than competitive systems ($250,000-$450,000). Competitive systems do not provide for recovery of reusable MEK. Evaluated as a solvent recovery system, the supercritical CO_2 system has a payout of less than one year.

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III. RECOMMENDATIONS

Further process studies integrated with experiments should be undertaken. For example, a design with liquid instead of supercritical CO_2 might have a lower capital cost than the supercritical design case, but experiments would be necessary to ascertain the parameters which determine the variable costs, e.g., amount of CO_2 regenerant necessary to achieve acceptable carbon working capacity.

A pilot unit should be built and operated to demonstrate the process at a larger scale. In addition to regenerability of the carbon, the unit should determine attrition losses due to transport with several grades of carbon, including fluid-bed carbons.

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IV. PROBLEM DEFINITION: VOLATILE-ORGANIC-COMPOUND EMISSIONS AND CONTROL METHODS

Volatile-organic-compound (VOC) emissions to the atmosphere are well-recognized as one of the two major contributors to photochemical smog. Together with nitrogen oxides (NO_x), these photochemically active compounds, or "oxidants", form smog at temperatures above 68°F whenever the VOC-to-NO_x ratio lies outside a certain range. Potentially more significant than the smog problem is the development of concern about benzene as a carcinogen. Many uncontrolled VOC vapors contain benzene: gasoline is a prime example. This concern may result in significantly more stringent emission controls than presently envisioned.

Specific measures to reduce hydrocarbon emissions from mobile sources (largely automobiles), are well underway. Stationary-source control is at various stages of accomplishment, depending on the nature of the source. Table IV.1 gives a breakdown of stationary sources, along with estimates of annual quantities of emissions nationally. The important groups of sources for which emission control is scheduled are solvent evaporation of various origins (especially surface coating operations), degreasing, and printing; the petroleum industry, particularly in marketing operations such as gasoline service stations; and organic chemicals manufacturing. Other major sources such as fuel combustion, open burning, and solid waste disposal have no specific control schedules at this point (Denny, 1978).

A. GASOLINE VAPORS

Under the Clean Air Act, a series of regulatory steps are underway to reduce gasoline vapor emissions, and these steps differ depending on the emission source. Bulk terminal facilities and service station underground storage tanks have been categorized as "Stage I" controllable sources under the Act. Within certain specified urban areas, found to be in "non-attainment for oxidants," the designation "Stage I" applies to those sources which must meet control criteria using "all reasonable

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TABLE IV.1

STATIONARY SOURCES OF VOLATILE ORGANIC COMPOUNDS

Source Category			Emissions, 10^6 Metric Tons/Yr.
1.	Solvent Evaporation		
	a)	Surface Coatings	
		1) Automobiles, Cans, Metal Coils, Paper and Fabric Products	0.90
		2) Other Industrial	0.30
		3) Architectural and Miscellaneous	0.30
		4) Flatwood Paneling Manufacture	0.05
		5) Miscellaneous Metal Parts and Products	0.20
		Surface Coatings Subtotal	1.75
	b)	Degreasing	0.70
	c)	Graphic Arts (Printing)	0.40
	d)	Dry Cleaning	0.25
	e)	Adhesives	0.20
	f)	Auto Refinishing	0.15
	g)	Other Solvent Use	3.0
		Solvent Evaporation Subtotal	6.45
2.	Petroleum and Natural Gas Industry		
	a)	Natural Gas and Crude Oil Production	0.20
	b)	Refinery Vacuum Systems, Wastewater Separators, and Process Unit Turnarounds	0.70
	c)	Refinery Fugitive Emissions	0.15

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TABLE IV.1
(Continued)

Source Category		Emissions, 10^6 Metric Tons/Yr.	
d)	Natural Gas and Natural Gasoline Plants	0.15	
e)	Liquid Storage Tanks, Fixed Roof	0.70	
f)	Service Stations, Stage II	0.50	
g)	Service Stations, Stage I	0.40	
h)	Bulk Gasoline Terminals	0.25	
i)	Gasoline Bulk Plants	0.15	
j)	Liquid Storage Tanks, Floating Roof	0.15	
k)	Ship and Barge Transport of Gasoline and Crude Oil	0.06	
Petroleum and Natural Gas Industry Subtotal			3.41
3. Organic Chemical Manufacture			
a)	Fugitive (leaks)	0.60	
b)	Process Streams	0.45	
c)	Storage and Handling	0.30	
d)	Waste Disposal	0.15	
Organic Chemical Manufacturing Subtotal			1.50
4. Other Manufacturing			
a)	Wood Furniture	0.20	
b)	Rubber Products	0.15	
c)	Metal Furniture	0.10	
d)	Vegetable Oils	0.07	
e)	Pharmaceuticals	0.05	
f)	Large Appliances	0.035	
Other Manufacturing Subtotal			0.61
5. Other, and Non-Itemized			
a)	Cutback Asphalt Paving	0.70	
b)	Magnet Wire Insulation	0.01	

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TABLE IV.1
(Continued)

Source Category		Emissions, 10^6 Metric Tons/Yr.
c) Non-itemized: Metals Manufacture; Other Manufacture; Fuel Combustion; Forest Agricultural, and Other Open Burning; Solid Waste Disposal.	4.0	
Other and Non-Itemized Subtotal		4.71
TOTAL		16.7

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measures" by July, 1982, a date mandated by the Clean Air Act. Still further control may be required by 1987 in certain areas depending on air quality and degree of urbanization.

Gasoline vapor emissions resulting from vehicle refilling have been categorized as a "Stage II" source. Such sources are subject to "study of the feasibility of controls," rather than being required to deploy "all reasonable measures." However, specific action is now being held in abeyance until the issue of benzene emission controls is resolved.

Gasoline Vapor Control Methods

The State of California has already enacted and enforced air-pollution control regulations which have caused gasoline service-station operators to install systems both for storage-tank (Stage I) and vehicle-refilling (Stage II) vapor emissions. As shown in Table IV.1, storage-tank emissions result from displacement of vapors during tank filling and from breathing.* Vehicle filling causes displacement losses from the vehicle gas tank, plus smaller losses due to spillage. Vapor balance systems have been installed on storage tanks alone to control that source, or together with special vehicle-fill nozzles to contrl both sources. The two most common types of vapor processing units are incinerators and carbon canisters. Many systems have been patented, as summarized in Table IV.2, some involving combinations of these types with each other or with other technology such as refrigeration or absorption. Incinerators suffer two drawbacks: they destroy the hydrocarbon, and thus eliminate a source of credit to defray operating costs; and they are a safety concern as a high-temperature combustion unit present at a gasoline station. Units containing granular activated carbon readily adsorb hydrocarbon vapors selectively from vent gas. When the adsorbent becomes saturated, the adsorbed vapors are stripped and the adsorbent regenerated in one of two ways: by pulling a

* Breathing refers to venting losses due to daily expansion of vapors in the tank free-board with the diurnal temperature rise. When the temperature falls, additional air is sucked in through the vent pipe, causing further gasoline vaporization in order to maintain vapor-liquid equilibrium.

TABLE IV.2

ISSUED PATENTS:

GASOLINE VAPOR DISPOSAL AND/OR RECOVERY

PROCESS	OWNER (INVENTOR)	REFERENCE	DESCRIPTION
Adsorption	Shell Oil, Houston (Katlen and Gwyn)	USP 3,897,193 (1975); also USP 3,979,175 (1976)	From storage tanks, vapors adsorbed, adsorbent regenerated by back-flushing with incineration of desorbed vapors.
Adsorption	No assignment given (Burtis and Babcock)	USP 3,907,010 (1975)	Storage tank vent vapors adsorbed, adsorbent regenerated with steam.
Adsorption	Shell Oil, Houston (McAndrew)	USP 3,902,874 (1975)	Storage tank vapors, released during filling, adsorbed, adsorbent regenerated by heated air back-flush, desorbed vapors fuel an internal combustion engine.
Adsorption	Shell Oil, Houston (Knowles)	USP 3,867,111 (1975)	Vapors adsorbed, adsorbent regenerated at reduced pressure without heat, desorbed vapors return to storage tank.

TABLE IV.2
(Continued)

PROCESS	OWNER(INVENTOR)	REFERENCE	DESCRIPTION
Adsorption	Calgon (Stoneburner and Joyce)	Brit. P. 1,359,703 (1974)	Vapors from fuel-delivery nozzle adsorbed by GAC in canister at the nozzle or remote.
Adsorption	Gulf R&D, Pittsburgh (Kramer and Mitchell)	USP 3,776,283 (1973)	During filling of storage tank from truck, vapors displaced via a line between tank and truck, adsorbed in an in-line canister.
Refrigeration	No assignment given (Pohl)	Ger. Off. 2,411,601 (1975)	Vapors condensed by direct or indirect heat exchange with liquid nitrogen.
Refrigeration	GATX (Mair)	USP 3,894,942 (1975)	Vapor first saturated by stripping liquid gasoline, then condensed with multi-stage compression and refrigeration.
Refrigeration	Tsukishima Kikai Co. (Honda)	Jap. Kokai 74;134,704 (1974)	Vapor first saturated by stripping liquid gasoline, water vapor adsorbed to lower dew point, vapor then chilled to condense liquid.
Refrigeration	No assignment given (Parker)	USP 3,778,968 (1973)	Petroleum storage-tank vapors refrigerated via contact with brine or glycol solution.
Absorption	Maruzen Eng. (Kajiura and Yashima)	Jap. Kokai 77;53,902 (1977)	Storage-tank vapors absorbed with kerosene, kerosene distilled to recover gasoline.
Absorption	Alar Eng. (Doncer and White)	USP 3,861,890 (1975)	Bulk station vapors absorbed in light oil, distilled for recovery.

vacuum and exhausting the concentrated stripped vapors to the storage tank; or by flow of stripping air through the carbon bed. Various concepts have been described for treating this relatively concentrated stream of vapors by refrigeration, absorption, or incineration. From a practical viewpoint, however, activated carbon systems are considered too expensive. Thus, new adsorption/regeneration concepts are needed before the method can be broadly used at service stations.

B. SOLVENT VAPORS

The principal sources of volatile organic compounds (VOC) emissions from evaporation of solvents are listed in Table IV.1. Sources are quite varied, and involve a variety of different volatile solvents. The source producing the single largest quantity of emissions is degreasing, comprising about 10% of all solvent emissions. The applicable Control Techniques Guidelines from EPA were issued in 1977, and carbon adsorption units are already in use (Larson, 1974; Enncking, 1973; and Shaw, 1975). A discussion of industrial VOC contaminants is given in further detail in Section VI, including criteria of selection of two compounds chosen for study in this program.

Solvent Vapor Control Methods

Numerous control techniques have been applied to the cleanup of VOC emissions, including solvent scrubbing, refrigerated condensation, incineration, catalytic incineration, and activated carbon adsorbers. These different techniques have widely varying efficiencies and economics; for many VOC streams, it is believed that carbon adsorption units offer the most economical operation and have the greatest potential for achieving over 95% emissions control (Foster-Miller, 1980). The discussion below focuses on carbon control techniques.

The equilibrium loading of GAC decreases with increasing carbon temperature and also decreases with decreasing solvent partial pressure. Thus, GAC can be regenerated by raising its temperature, with steam or hot-inert gas, for instance, or by reducing the solvent partial pressure, by pulling a vacuum, for example. In the case of thermal regeneration, the steam or hot gas heats up the carbon, provides the heat of desorption, and also creates sufficient mass flux through the bed to sweep out the desorbed compound. In the case of vacuum regeneration, the carbon tends to cool during desorption, unless some indirect heating means is employed (heat exchangers in the carbon bed, for instance).

Steam is the most common method for thermally regenerating GAC. It has a high heat transfer coefficient and a high latent heat of condensation which make it efficient for heating the carbon. Steam is also often readily available at the process site. There are several disadvantages of steam, however, including the potential of corrosion problems created by the steam/carbon system, possible catalysis of undesirable chemical reactions such as polymerization of monomers, formation of acids, etc., and the necessity of a distillation system to recover any water-soluble desorbate from the condensed steam.

The amount of steam necessary to achieve a given degree of regeneration is a function of the nature of the adsorbate; in general, the fractional degree of regeneration is an s-shaped function of the mass of steam used per unit mass of carbon. For example, for methylene chloride, representative of a relatively weakly adsorbed compound, 20% of the carbon working capacity is recovered with 0.19 lbs steam/lb carbon, 80% with 0.21 lbs/lb, 90% with 0.39 lbs/lb, and 95% is recovered with 0.61 lbs steam/lb carbon (Basdekis, 1980). A trade-off exists between working capacity and effluent quality versus steam requirement.

Hot-gas regeneration is accomplished by sweeping an inert gas through the GAC bed. Convective heating of the carbon can be supplemented with conductive heating from a heat exchanger or heating element. The absence

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of water allows this system to be used with water-soluble organics, and permits the use of less expensive materials of construction in the vessel fabrication because of the low-corrosion environment. The primary disadvantage of this regeneration process is that there is a build-up of higher molecular weight compounds on the carbon, resulting in a low working capacity.

In vacuum regeneration systems, the GAC bed is evacuated to a pressure of a few mm Hg to affect the desorption. The advantage of this scheme is that the moderate temperatures enable a variety of heat-sensitive compounds (such as monomers) to be handled.

Activated carbon vapor control units have either fixed- or fluidized-bed adsorber configurations. Fixed-bed carbon units are loaded with commercial GACs, which typically have carbon particle size ranges of 4x10, 6x16 or 12x30 U.S. mesh. The carbon beds are shallow to avoid large pressure drop; superficial velocity of the VOC stream is usually limited to the range of 50-100 ft./min. The fixed-bed units operate in a batch-continuous manner-- VOC-containing air is flowed through one carbon bed while the other(s) is being regenerated. When the regeneration cycle of one bed is complete, the VOC-containing air is diverted to it and the VOC-loaded bed undergoes regeneration. There are at least four manufacturers of fixed-bed carbon units in the United States today.

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The Kureha Chemical Co. (Japan), has developed a fluidized-bed carbon system, marketed in the U.S. by Union Carbide. A special attrition-resistant spherical vapor-phase carbon produced from petroleum pitch contributed to the development of this process. The adsorber and desorber are one vessel; the top is a multistage fluidized-bed adsorber and the bottom is a moving, dense-bed regenerating section. VOC-containing feed at a superficial velocity of approximatley 200 ft./min. enters below the fluidized bed, travels up through the perforated trays and exits from the top. Carbon flows counter-currently to the air and drops continuously into the regeneration section where it forms a dense bed preheated by a heat ex-

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changer. Carbon that has been regenerated is cooled by another heat exchanger and cycled back up to the top of the adsorber. In practice, the fluidized-bed can permit more uniform vapor contacting and heat distribution and is thus potentially more efficient than a fixed-bed system.

Table IV.3 presents a summary of capital and operating costs for GAC and alternate processes for VOC control. Cost figures shown have been updated to December, 1980.

The first item gives cost information for fixed-bed steam-regenerated GAC systems described by Basdekis (1980). The capital cost of $385,000 to $440,000 for the 10,000 SCFM system is about 1.4 times that of the 5,000 SCFM system; this does not include off-site equipment for steam generation. The variable cost is intended to be for a generalized VOC case, with a steam utilization of 0.3 lbs/lb GAC.

Cost data from Foster-Miller (1980) cover refrigeration, incineration, and fixed and fluidized-bed GAC systems for treating 5,000 SCFM of air. The variable costs for the carbon systems include steam utilization of 0.7 lbs/lb GAC for the fixed bed arrangement and 0.3 lbs/lb GAC for the fluidized bed.

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A third figure for a fixed-bed GAC system is given based on published information (McGill, Inc., 1980) pertaining to isobutane vapor adsorption and recovery; it is equivalent to an 8,800 SCFM system. The bed regeneration method consists of combined vacuum and hot-gas regeneration steps.

It is apparent that capital and operating costs at comparable capacity vary significantly among the systems described (e.g., capital cost of $175,000 to $310,000 for fixed-bed carbon systems at 5000 SCFM capacity). For a given solvent feed rate, feed concentration, effluent concentration, and recovered solvent value, the payout periods for the different systems range from less than one year for a carbon system to infinity for an incineration system (Foster-Miller, 1980).

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TABLE IV.3

COMPARATIVE ECONOMICS OF
VOC CONTROL SYSTEMS

EPA 6802-2577
H.S. Basdekis

Installed Capital Cost
(Adjusted to 12/80; Original Basis: 12/79)

	5000 SCFM	10,000 SCFM	Variable Costs† 5000 SCFM
Fixed Carbon Bed	$275-310 K	$385-440 K	$ 13 K

EPA 6802-3134
Foster-Miller

Installed Capital Cost
(Adjusted to 12/80; Original Basis: 8/79)

	5000 SCFM	Variable Costs† 5000 SCFM
Refrigeration	$575 K	$138 K
Incineration	175	173
Fixed Carbon Bed	175	32
Fluidized Carbon Bed	250	11

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McGill, Inc., Chem. Eng., 87(17), 49(1980).
McGill, Inc.

Installed Capital Cost
(Adjusted to 12/80; Original Basis: 8/80)

	8800 SCFM*
Fixed Carbon Bed	$ 460 K

(*Original Basis: 220 SCFM 19% isobutane, Equivalent flow at 1/4 of LEL (LEL = 1.9%) = 8800 SCFM)

†Variable Cost Bases: Electricity $0.05 KWH; Fuel $3.50 MMBTU; Steam $4.50 MMBTU; Water $0.15 MGAL; Carbon $1.25 lb.

V. PREVIOUS WORK WITH SUPERCRITICAL-FLUID REGENERATION OF GAC

That supercritical fluids can regenerate carbon (and other adsorbents) loaded with a wide range of adsorbates has been demonstrated in a development program at Arthur D. Little during the past three years*. Liquid-phase adsorbents (including commercial GAC's, developmental GAC, commercial powdered activated carbon and commercial synthetic resin adsorbents) loaded with test adsorbates from aqueous solutions (including five pesticides -- primarily complex substituted aromatics, acetic acid and phenol) have been effectively regenerated with supercritical carbon dioxide.

Figure V.1 shows adsorption-breakthrough curves for a series of thirty-one adsorption/regeneration cycles with an alachlor (2-chloro-2'-2' diethyl-N-(methoxymethyl) acetanilide) adsorbate. Alachlor is a herbicide with behavior characteristics of strongly adsorbed solutes**. In the first several cycles, the carbon working capacity (determined by integrating the area above the curve) declined to 50-60% of that of the virgin carbon (indicated in Figure V.1 by the decrease in area above the adsorption curves). With subsequent cycles, however, there was virtually no further decline in capacity.

Carbon loaded with acetic acid could be completely regenerated with supercritical CO_2. Adsorption breakthrough curves for an eight-cycle test with acetic acid adsorbate, presented in Figure V.2, show that there was no decline in carbon capacity over the test duration.

Carbon loaded with phenol underwent a decline in working capacity of 20-30% with the first several cycles. Working capacity data for alachlor, acetic acid and phenol adsorbates are tabulated in Table V.1.

*EPA Cooperative Agreement #CR806-874-01

**The adsorption curves in Figure V.1 breakthrough rapidly because feed flowrate was accelerated to decrease the time required for adsorption. Such rapid breakthrough curves are not indicative of the highest achievable effluent quality.

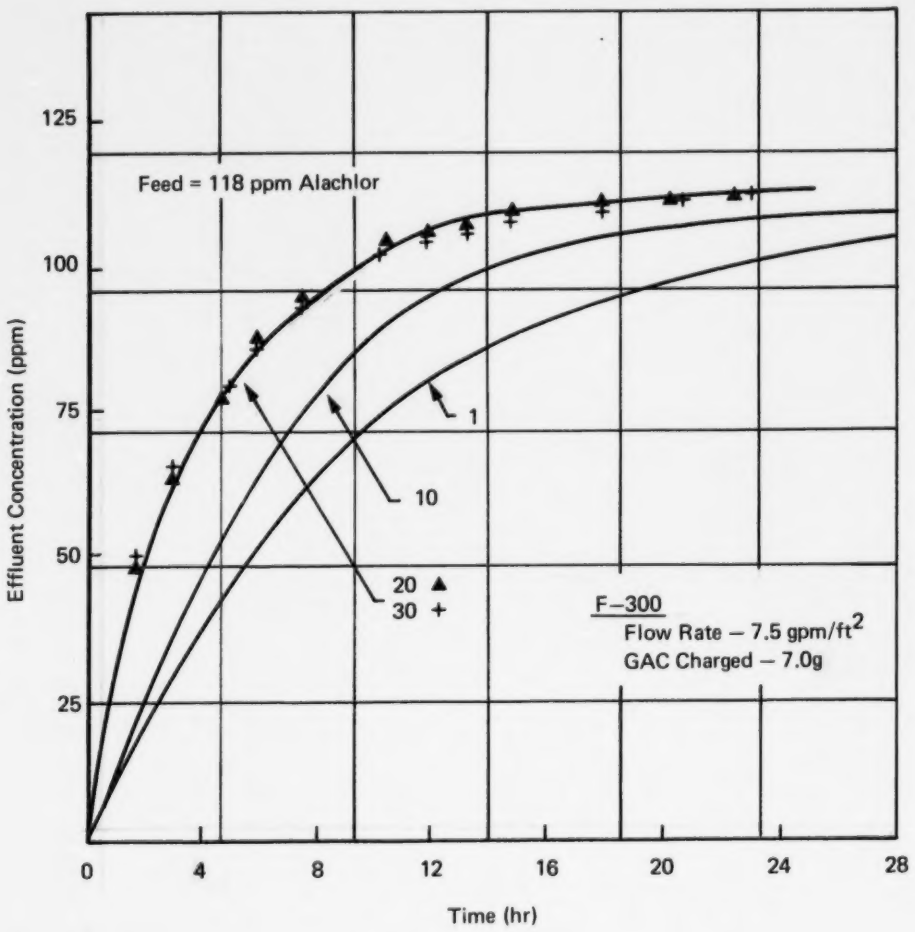

FIGURE V.1 ADSORPTION OF ALACHLOR ON F–300
(NUMBERS ON CURVES REFER TO ADSORPTION CYCLE)

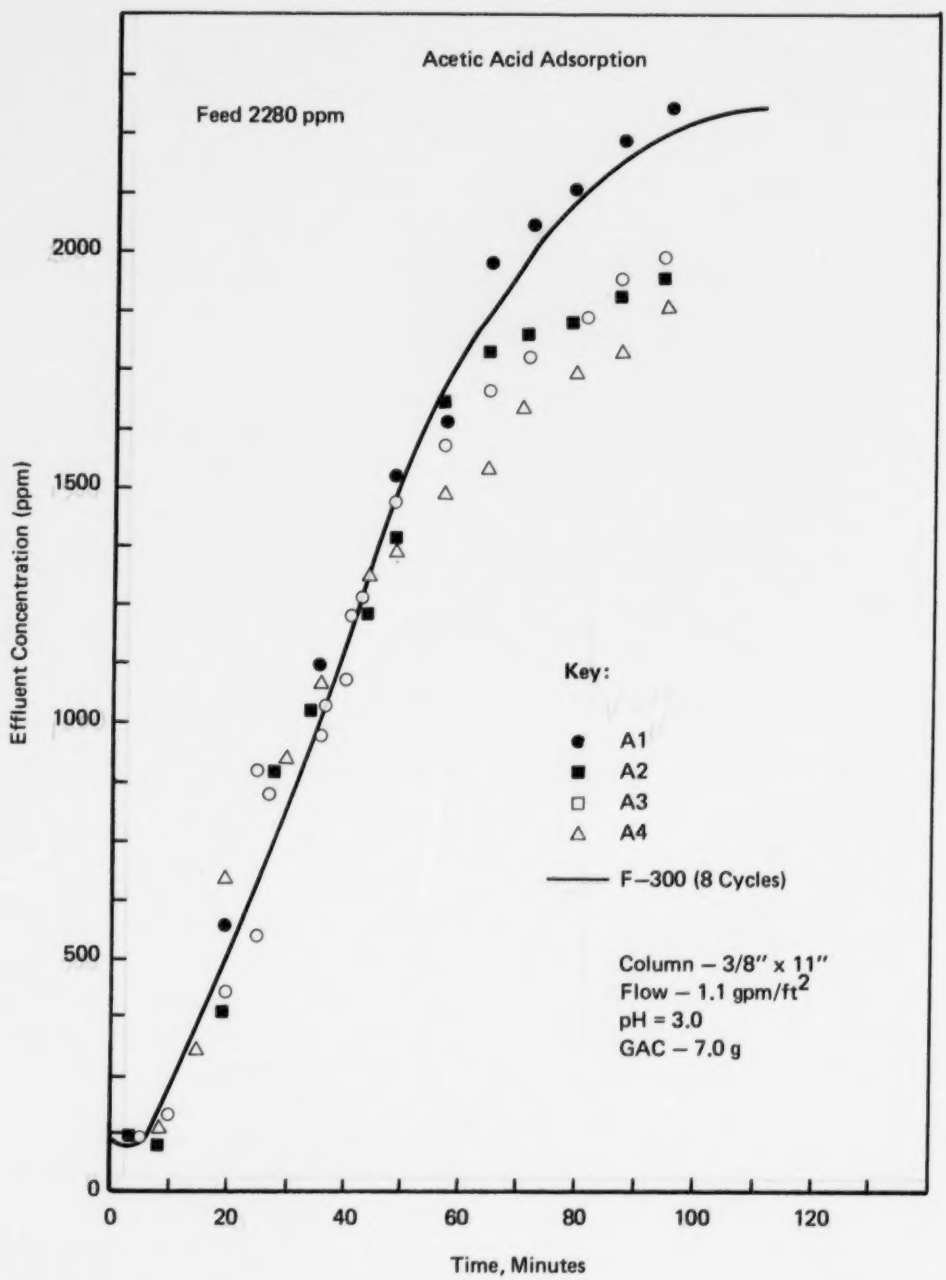

FIGURE V.2 ADSORPTION OF ACETIC ACID ON F–300

TABLE V.1

SCF CO_2 REGENERATION OF GAC: SUMMARY OF OPERATING CONDITIONS AND RESULTS

EXPERIMENT NO.	1	2	3	4	5	6	7
Type of carbon	F-300	F-300	CC-1230	GX-31	XE-348	F-300	F-300
Solute	Phenol	Phenol	Phenol	Phenol	Phenol	Acetic Acid	Alachlor
Weight of adsorbent (g)	0.37	7.0	7.0	4.0	7.9	7.0	7.0
Mesh size	-100 +120	+20	N/A	-16 +30	-20 +50	+20	+20
ADSORPTION							
Feed conc. (ppm)	10,000	2,380	2,380	2,380	2,380	2,380	118
Flow rate (gpm/ft^2)	0.3-1.0	1.1	1.1	1.1	1.1	1.1	7.5
($l/sec\ m^2$)	0.2-0.7	0.7	0.7	0.7	0.7	0.7	5.1
DESORPTION							
Temp. (^oC)	55	120	120	120	70	120	70-120
Pressure (psig)	2200-2800	2200	2200	2200	2200	2200	4000
(MPa)	15.2-19.3	15.2	15.2	15.2	15.2	15.2	27.6
CAPACITY (g/g)							
Cycle No.							
1	0.35	0.19	0.21	0.50	0.17	0.048	0.20
2	0.25	0.16	0.18	0.44	0.15	0.043	
3	0.24	0.15	0.18		0.12	0.044	
4	0.24	0.16			0.13	0.045	
5	0.25				0.14	0.046	
6	0.26					0.044	
7	0.23					0.045	
8	0.22					0.050	
10							0.15
20							0.10
30							0.10

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In addition to the multiple cycle adsorption/desorption studies, the ability to operate the SCF carbon regeneration process in a closed-loop mode with recycle CO_2 was investigated. Separation experiments were run to determine whether the high-pressure CO_2 stream laden with several percent of dissolved adsorbate could have its adsorbate concentration lowered by reducing the pressure. Studies with alachlor showed that the separation predicted from equilibrium solubility measurements at lower pressures was indeed achieved in a reduced-pressure separator run under flow conditions. Moreover, small-scale closed-loop systems were operated, recycling CO_2 which was purified in the single-stage separation. GAC was successfully regenerated in this closed-loop system.

The carbon desorption dynamics were modeled using local equilibrium theory (LET). This theory assumes that the diffusion of solute out of the SCF-filled pores and from the external surface of the adsorbent particle into the bulk SCF phase is sufficiently rapid for equilibrium to exist between adsorbent particles and the adjacent fluid at all points within the column (Sherwood, et al. 1975). The desorption dynamics of alachlor from F-300 GAC with CO_2 at 55°C and 150 atm were well modeled by the LET; the Langmuir constants which gave the best agreement between the theoretical and experimental desorption curves are q_m= 0.203 g alachlor/g carbon and K = 1910 cm^3/g.

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The local equilibrium model is a valuable tool: once the CO_2 regenerant/GAC adsorbate isotherm is known (e.g., for the CO_2-alachlor system, a Langmuir isotherm relationship was determined) desorption performance for any size column can be predicted, and thus scaled-up systems can be designed. Experimentally measured desorption dynamics for GAC columns 1.22-m in length and 3.2-cm-ID are in reasonable agreement with LET desorption predictions based on data from 0.23-m-L, 1.0-cm-ID columns.

The prior work described above was focused on adsorbates sparingly soluble in the regenerating solvent. One of the purposes of the current

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study was to test the process for more soluble organic materials, and to consider process design changes that would take into account these differences in systems properties.

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VI. ADSORBATE AND ADSORBENT SELECTION

A. SELECTION OF INDUSTRIAL VOLATILE ORGANIC COMPOUNDS

Several sources were consulted to aid in the selection of two industrial volatile organic compounds (IVOC's). These sources included the report "End Uses of Solvents Containing VOC's," (Ostojic, 1979), the draft report, "Source Assessment Overview Matrix for National Criteria Pollutant Emissions," (Eimutis, 1978), and the New Source Standard Priority List (Code of Federal Regulations).

The OAQPS recommended that water-soluble solvents be given serious consideration because of the water-solvent separation problem which is created when steam is used for the carbon regeneration.

Methyl ethyl ketone (MEK) and ethyl alcohol were chosen as the industrial volatile organic compounds. They were selected from a group of ten major oxygenated industrial solvents: acetone, n-butanol, n-butyl acetate, ethanol, ethyl acetate, glycol ethers, isopropanol, methanol, MEK and methyl isobutyl ketone (MEK). Hydrocarbon VOC's were excluded because their behavior would be similar to gasoline vapor which was selected separately as an adsorbate of interest. Chlorinated hydrocarbons (e.g., methylene chloride, perchloroethylene) were also excluded because current technology for regenerating GAC loaded with these compounds appears to be satisfactory. Chlorinated hydrocarbon solvents are insoluble or very slightly soluble in water. In a steam regenerated GAC system they would not, therefore, have the VOC/water separation problem that a water-soluble compound (e.g., an oxygenate) would.

Selection of the two IVOC's was based on comparison of the following for the ten oxygenates: solvent demand in millions of pounds per year, solubility in water, azeotrope formation with water, volatility and toxicity. These quantities are tabulated in Table VI.1.

TABLE VI.1

PROPERTIES OF TEN INDUSTRIAL OXYGENATED ORGANIC SOLVENTS

SOLVENT	SOLVENT DEMAND* 10^6 lb/year	(demand date)	SOLUBILITY IN H_2O	AZEOTROPE WT % SOLVENT	BOILING PT. °C	TOXICITY
Acetone	230 protective coatings	(5/79)		None	56	Very low
n-Butanol	130 nitrocellulose lacquers	(6/79)	9% (15°C)	62	118	Irritant to E.N.T.
n-Butyl Acetate	50 nitrocellulose coatings	(8/78)	0.7%	71	126	Irritant to E.N.T.
Ethanol	380 190 protective coatings 190 cleaning preparations	(10/78)	∞	96	78	
Ethyl Acetate	160 coatings, inks adhesives	(12/78)	8.5% (15°C)	94	77	Irritant to E.N.T.
Glycol Ethers (Cellosolves)	290 260 protective coatings 30 inks	(4/78)	∞	-	>125	Relatively low
Isopropanol	200 protective coatings	(2/78)	∞	88	82	
Methanol	(670) total solvent use	(8/79)	∞	None	65	Very toxic
MEK	490 230 PVC coatings 115 other coatings 85 adhesives 60 nitrocellulose lacquers	(4/79)	35% (10°C)	89	80	Irritant. Unpleasant odor.
MIBK	120 65 vinyl coatings, inks, adhesives 55 nitrocellulose lacquers	(10/78)	2% (20°C)	76	118	Not highly toxic.

*Demand and toxicity data compiled from "Chemical Products Synopses," (1978,1979)

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The acetates have the lowest water solubilities (<8.5% at 15°C), and the glycol ethers (cellosolves) have relatively low volatilities and toxicities. Thus, these compounds were deemed to be of lower priority than the ketones or alcohols.

MEK's demand (490 mm lb/yr) is the highest of the ketones -- more than twice that of acetone (230 mm lb/yr) and over four times that of MIBK (120 mm lb/yr). Although MEK's solubility in water (35% to 10°C) is less than acetone's (infinite solubility), MEK forms an azeotrope with water which makes their complete separation by distillation more difficult than the acetone/water separation. Also, MEK is more toxic than acetone and hence there is greater incentive to remove it from the air. MEK was thus considered to be the highest priority ketone and was selected as one IVOC.

Ethanol's demand (380 mm lb/year) exceeds that of isopropanol (200 mm lb/yr) by about a factor of two, and that of n-butanol (130 mm lb/yr; only 9% solubility in water) by approximately a factor of three. The demand listed for methanol (670 mm lb/yr) is for total solvent usage, including extraction and crystallization; its demand as an industrial coating solvent is considerably less. While methanol is more toxic than ethanol, it does not form an azeotrope with water, as ethanol does. Ethanol was, therefore, considered to be the highest priority alcohol and was selected as the second VOC.

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B. SELECTION AND CHARACTERIZATION OF GAC

Marked differences in vapor working capacities have been noted among different manufacturers' GAC's, and even among different batches of one manufacturer's GAC (Manos and Kelly, 1977). For instance, with gasoline vapor, a Westvaco 14x35 mesh had a 0.113 g/g carbon capacity, and an I.C.I. 12x30 mesh had a 0.041 g/g carbon capacity, a factor of 2.8 difference. Taking the apparent densities of the carbons into account, 0.31 and 0.41 g/cc for the Westvaco were I.C.I. carbons, respectively, the working capacities were 0.035 and 0.017 g/cc, respectively, a factor of two difference.

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Various GAC manufacturers were contacted to obtain information about their products, specifically vapor-phase material. On the basis of published data (Manos & Kelly, 1977) and some preliminary investigation, it was anticipated that extremes in working capacity would be found between low-density high-surface-area carbons and higher-density lower-surface area carbons.

The actual carbon samples considered for use in the adsorption/regeneration experiments were characterized by measurement of the following parameters: density, surface area, pore volume, and pore-size distribution. Arrangements were made with the Department of Chemical Engineering at Tufts University to have surface-area and pore-size-distribution measurements made on the granular activated carbon samples.

Using a Quantachrome Company's Quantasorb continuous-flow adsorption system with N_2/He gas mixtures, a three-point adsorption isotherm was measured at pressures P below $P/P_0 = 0.35$ (where P_0 is the saturation pressure of the adsorbate gas at the system temperature), and a multi-point desorption isotherm was measured at pressures ranging from 0.99 P_0 to approximately 0.3 P_0. The three-point adsorption data was used in the Brunauer-Emmett-Teller (B.E.T.) procedure for calculating specific surface area; the desorption data was used to establish the average pore volume and pore size distribution.

Surface area and pore volume analyses were performed on two Calgon commercial vapor-phase carbons, type BPL (coal-based) and PCB (coconut shell), one Calgon liquid-phase carbon, type F-300, and an Amoco experimental high-surface-area carbon, type GX-31. Results are shown in Table VI.2. The experimentally-determined surface area data for the Calgon carbons, 980, 1140 and 1270 m^2/g for the F-300, PCB and BPL carbons, respectively, are in good agreement with the manufacturer's quoted valves (Calgon Corp.). The pore volume data are also in accord with the manufacturer's valves, with the exception of the PCB carbon.

TABLE VI.2

EXPERIMENTALLY DETERMINED PHYSICAL PROPERTIES OF FOUR ACTIVATED CARBONS

GAC	BET AREA m^2/g	TOTAL PORE VOLUME cm^3/g	MEAN PORE DIAMETER Å	PORE VOLUME DISTRIBUTION Diameter: <20Å	20-40Å	>40Å
Calgon BPL 12 x 30 mesh (vapor phase)	1270 (1050-1150)*	0.62 (0.7)	17	52%	33%	15%
Calgon PCB 12 x 30 mesh (vapor phase)	1140 (1150-1250)*	1.20 (0.72)	31	77%	11%	12%
Calgon F-300 12 x 30 mesh (liquid phase)	980 (950-1050)	0.6 (0.85)	24	41%	52%	7%
Amoco GX-31 (Pellet) (experimental)	2240	0.43	21	53%	8%	39%

*Values in parentheses are Manufacturer's quoted values (Calgon Corp.).

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The BPL and PCB carbons, which are intended for vapor phase applications, have a large fraction of their surface area in pores less than 20Å in diameter. Because of rapid diffusion in the vapor phase, it is not necessary for a vapor-phase carbon to have a large proportion of its surface area in "channel"-sized pores (20-40Å).

The liquid-phase F-300 has a larger percentage of its surface area in pores in the 20-40Å range; liquid diffusivities are lower than those in the vapor phase which necessitates having more "channel"-sized pores. Analysis of the pore size distribution of the GX-31 shows that it is vapor-phase-like, with 53% of its pore volume in pores in the 20-40Å range.

Calgon type BPL GAC was chosen as the carbon for the experimental work of this investigation. This GAC was chosen because it is in widespread use in commercial vapor-phase applications; more so than type PCB. Amoco GX-31 is not presently in commercial use.

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VII. GASOLINE AND IVOC ADSORPTION/DESORPTION STUDIES

A. EXPERIMENTAL APPARATUS AND PROCEDURE

1. Adsorption System

The flow schematic for the GAC adsorption system is shown in Figure VII.1. The gasoline or IVOC carrier stream (Matheson Zero Air, 2.0 vol. ppm as CH_4, further treated by passing through a 120-cm-long glass column packed with desiccant, GAC and molecular sieves) was flowed through columns B1 and B2 to adjust the stream water partial pressure to the desired level. Water-filled gas bubbling column B1 and glass wool-filled* column B2 were immersed in a constant temperature refrigerated bath (Blue M, model MR-3210A-1) to adjust the water saturation temperature; saturation of the stream with water at 1 atm and 2°C for example, created a water partial pressure of 5.2 mmHg or a relative humidity of 23% at 24°C.

Constant humidity air was passed through flowmeter 1 and VOC/gasline-filled gas bubbling column C1 and passed through the glass fiber-filled column C2. This stream contained the gasoline or VOC at its saturation concentration. The VOC/gasoline stream could then be mixed with diluent, if desired and passed through the GAC adsorption column A or the GAC column by-pass. The GAC column was at the thermostated laboratory temperature, which varied not more than ± 1°C over one hour. The column was a 316-stainless-steel high-pressure tube 0.95-cm-ID by 23.5-cm-long loaded with Calgon BPL 12 x 30 mesh GAC.

The gasoline or VOC-containing streams were flowed through the carbon bed at various rates and concentrations, depending on the particular adsorbate. Typical rates and concentrations were 1 liter/min and 100,000 ppm by volume, respectively. Flow conditions reported in a published study (Manos and Kelly, 1977) could be achieved with this system.

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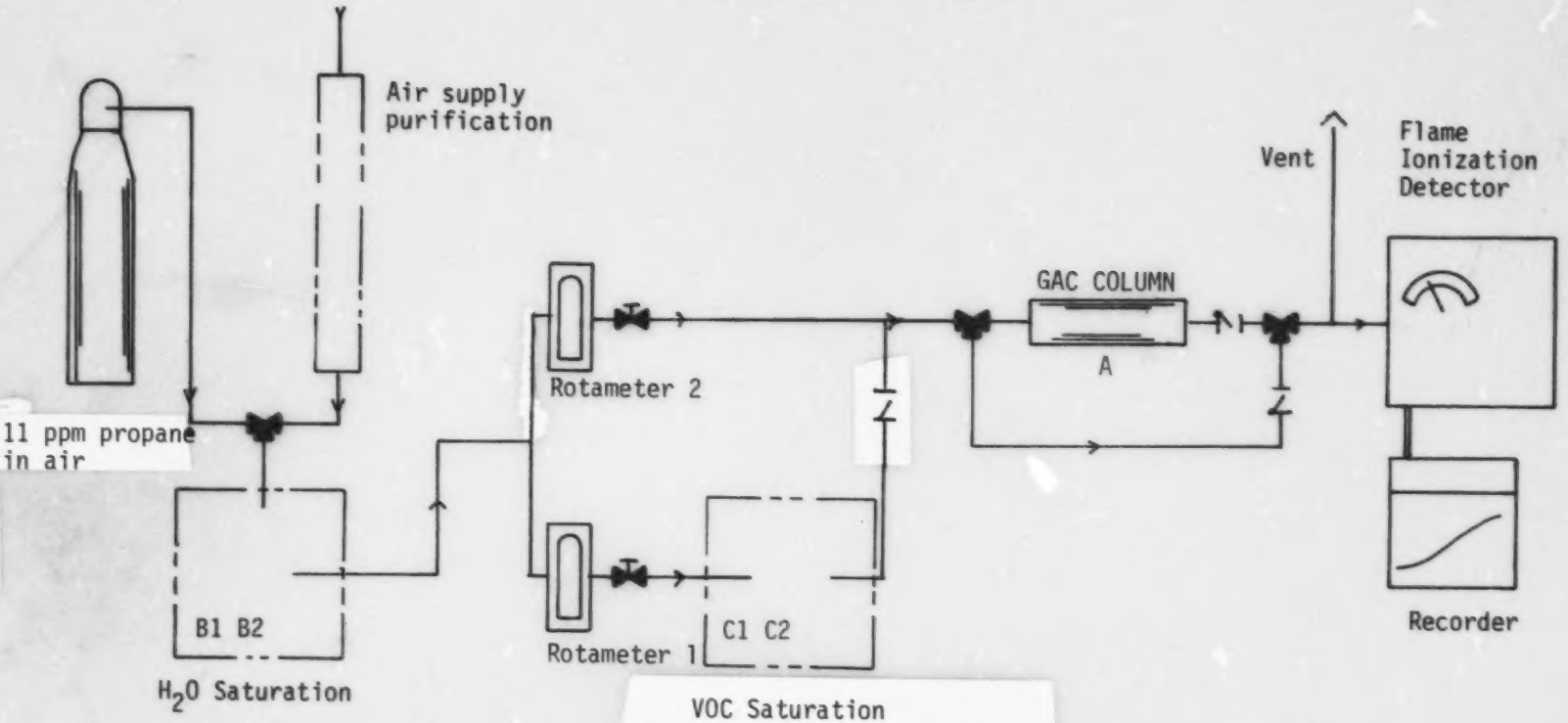
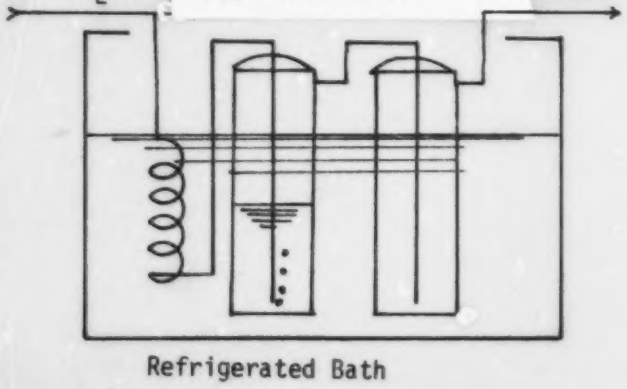
*glass wool was employed to remove entrained water droplets from the gas stream.

FIGURE VII.1

GAC ADSORPTION APPARATUS





GAC COLUMN SIZE

Diam. (cm)	Area (cm^2)	Length (cm)	Vol. (cm^3)
0.95	0.71	23.5	16.7

ROTAMETER SIZES

1. Matheson 602 or 603
2. Matheson 604

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The GAC column influent and effluent concentrations were monitored with a flame-ionization detector (FID) (Scott, model 415) connected to a strip-chart recorder. The FID was zeroed with the Ultra Zero Air and calibrated with 11 vol. ppm propane gas.

2. Regeneration System

After an adsorption was completed, the GAC column was transferred to the regeneration apparatus. The flow schematic for the regeneration apparatus is shown in Figure VII.2. Carbon dioxide (Cardox, 99.5%, with the balance N_2 and O_2, and with hydrocarbon content determined by FID as 5 vol. ppm as propane) was compressed to 103 atm with a diaphragm compressor (Aminco, Model 46-13421) and heated (typically to 50°C) in the reservoir upstream of the column. The heated pressurized stream was flowed through the GAC column, across the pressure let-down valve to either: a) the rotameter and dry test meter, to measure instantaneous flow rate and CO_2 volume or, b) the FID and dry test meter to monitor the VOC concentration as a function of CO_2 regenerant volume. The adsorption and desorption apparatus tubing and fittings were stainless steel.

3. Gasoline Vapor Composition

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In the VOC bubbling column, air strips gasoline of its lighter components. As a result, the liquid and vapor gasoline compositions change as a function of time. To determine the magnitude of this effect, a calculation of gasoline composition change as a function of weight-percent gasoline removed was made for 24°C and 1 atm total pressure, based on a gasoline composition given by Muller, et al. (1966); the results are given in Table VII.1.

The vapor mole fractions of the lighest components - isobutane, n-butane, isopentane and butenes - change appreciably as gasoline equilibrium vapor is removed. The vapor mole fractions of the heavier components (not shown) have a smaller change. In order to maintain a constant

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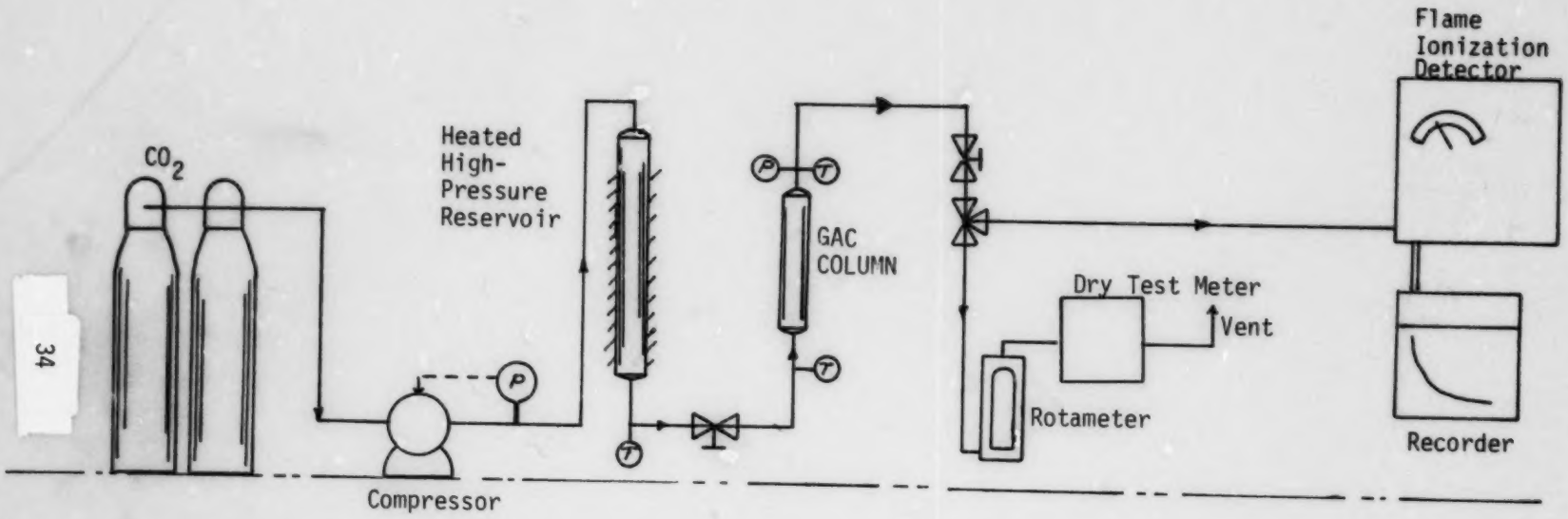
FIGURE VII.2

GAC REGENERATION APPARATUS



Typical Regeneration Conditions:

P = 1500 PSI
T = 50°C
Q = 20 standard liters/min CO_2
V = 100 standard liters

TABLE VII.1

Change in Vapor Mole Fractions of Light Components of Gasoline As a Function of Wt % Gasoline Removed (as Equilibrium Vapor) at 24°C and 1 atm Total Pressure

Wt % removed	0%	1%		2%	
"Partial pressure" of mixture, PSIA	7.0	6.8		6.5	
	Wt % in initial mixture	Cumulative Fraction Lost,%	Vapor Mol Fraction	Cumulative Fraction Lost,%	Vapor Mol Fraction
Isobutane	.05	8.9	.0023	17.4	.0021
N-Butane	6.40	7.0	.2344	13.8	.2204
Isopentane	13.20	2.6	.1495	5.3	.1475
Butenes	0.24	6.3	.0083	12.5	.0079

Wt % removed	3%	4%		5%	
"Partial pressure" of mixture, PSIA	6.3	6.0		5.8	
	Cumulative Fraction Lost,%	Vapor Mol Fraction	Cumulative Fraction Lost,%	Vapor Mol Fraction	Cumulative Fraction Lost,%	Vapor Mol Fraction
Isobutane	25.5	.002	33.1	.0018	40.2	.0016
N-Butane	20.4	.2065	26.7	.1928	32.8	.1793
Isopentane	8.0	.1453	10.8	.1430	13.6	.1406
Butenes	18.6	.0074	24.5	.0070	30.2	.0066

TABLE VII.1

(continued)

Wt % removed	10%		15%		20%	
"Partial Pressure" of mixture, PSIA	4.6		3.5		2.6	
	Cumulative Fraction Lost,%	Vapor Mol Fraction	Cumulative Fraction Lost,%	Vapor Mol Fraction	Cumulative Fraction Lost,%	Vapor Mol Fraction
Isobutane	69.2	.0009	87.3	.0004	96.3	.0001
N-Butane	59.8	.1157	79.7	.0631	92.1	.0265
Isopentane	28.4	.1256	44.3	.1057	60.7	.0810
Butenes	56.1	.0044	76.4	.0026	90.0	.0012

gasoline vapor composition for the adsorption experiments, a sufficiently large initial volume of gasoline was used so that no more than about 3 weight percent was removed during the experiment.

B. RESULTS

1. Screening Studies

A six-cycle adsorption/regeneration test on Calgon BPL 12x30 mesh GAC was carried out. A British Petroleum company 89-octane no-lead gasoline (purchased at a local service station) was used as the vapor source. Air saturated with the gasoline at temperatures between 22-24°C was flowed at approximately 500 cc/min through a 0.95-cm-diameter 23-cm-long high-pressure pipe packed with 7.5 g carbon. The adsorptions were not terminated at a particular breakthrough point, but rather at 30 minutes of adsorption time. Regenerations were run immediately after adsorption. The tests occurred over a six-day period, with the column open to the atmosphere when it was not adsorbing or being regenerated; the humidity of the air was not controlled. The carbon loadings, regeneration conditions and residual weights for each cycle are presented in Table VII.2.

The first three regenerations were run with liquid CO_2, but above the critical pressure. The 53 standard liters (SL) of CO_2 used in the third run left more residual on the carbon than did the 96 and 85 SL of CO_2 used in the first and second regenerations, respectively. The fourth regeneration was run with supercritical CO_2 and had the lowest residual, 0.013 g/g carbon. The working capacity for this cycle was 26.1 g/100 g carbon.

The fifth and sixth regenerations were run with Freon-13 (chlorotrifluoromethane; T_C = 28.9°C, P_C = 38.2 atm). The fifth regeneration with 92 SL of liquid Freon-13 at 24°C had a greater residual, 0.036 g/g carbon, than did the first cycle (96 SL of liquid CO_2 at 24°C, residual of 0.018 g/g carbon). The residual left by 108 SL of supercritical Freon-13, 0.015

TABLE VII.2

Six Cycle Adsorption/Regeneration Carbon
Calgon BPL 12x30 Mesh Gasoline = B.P. no-lead, 89 Octane

7.15 g GAC in column

Cycle	Loading & Residual		Regeneration Conditions
1	loading 1.98 g	0.277 g/g carbon	T = 24°C Liquid P = 1500 psi CO_2 96 SL @ 10 SL/min
	residual 0.13 g	0.018 g/g	
2	loading 1.99 g	0.278 g/g	T = 26°C Liquid P = 1600 psi CO_2 85 SL @ 10 SL/min
	residual 0.20 g	0.028 g/g	
3	loading 1.96 g	0.274 g/g	T = 24°C Liquid P = 1600 for 20 SL CO_2 P ∿ 1000 for 33 SL 53 SL @ 10 SL/min
	residual 0.31 g	0.043 g/g	
4	loading 1.96 g	0.274 g/g	T ∿ 50°C Supercritical P = 1600 psi CO_2 102 SL @ 10 SL/min
	residual 0.09 g	0.013 g/g	
5	loading 1.84 g	0.257 g/g carbon	T = 24°C Liquid P = 1200 psi CF_3Cl 92 SL @ 10 SL/min
	residual 0.26 g	0.036 g/g	
6	loading 1.93 g	0.270 g/g	T ∿ 50°C Supercritical P = 1200 psi CF_3Cl 108 SL @ 10 SL/min
	residual 0.11 g	0.015 g/g	

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g/g carbon, was very close to the 0.013 g/g carbon residual left by the supercritical CO_2.

These preliminary data showed that both liquid CO_2 and Freon-13 can effectively regenerate GAC which had adsorbed gasoline vapors, with CO_2 leaving a lower residual than Freon when approximately 100 SL are used. Supercritical CO_2 and Freon leave very low residuals when about 100 SL are used; supercritical CO_2 reduced the residual of 0.043 g/g, left after three cycles with liquid CO_2, to 0.013 g/g.

Preliminary testing was also done with the experimental GAC from Amoco, mentioned before as one of the GAC samples considered for use in this program. Air saturated at 23°C with the BP no-lead gasoline was flowed for 30 minutes through a 1.7-cm diameter 26-cm-length high-pressure pipe packed with 7.72 g of Amoco GX-31 pelletized 16-32 mesh carbon. The regeneration was run with 110 SL of supercritical CO_2 at 50°C and 1400 psi.

The working capacity was 0.60 g/g carbon. On the basis of gms gasoline/cc carbon, the capacity of the Amoco carbon was 0.6 g/g carbon x 0.248 g carbon/cc = 0.15 g/cc, whereas the Calgon carbon was 0.25 g/g carbon x 0.455 g carbon/cc = 0.11 g/cc, a factor of 1.4 difference. Results for the adsorption/SCF regeneration on GX-31 are summarized below:

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Loading and Residual	Regeneration Conditions
loading: 5.02 g; 0.650 g/g carbon	T ~ 50°C
residual: 0.39 g; 0.051 g/g	P = 1400 psi Supercritical CO_2
	110 SL @ 10 SL/min

When the activated carbon column was removed from the high-pressure desorption apparatus after regeneration, the glass fiber plug at the desorption-effluent end of the column was blackened with fines from the carbon. Work was terminated with the GX-31 carbon at that time.

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Toluene comprised up to 19 wt% of the heel formed during the 1000-cycle Manos and Kelly (1977) test. Thus, it was felt that the ability to desorb it from GAC would be a good indication of the ability of the near-critical fluid regeneration technique to maintain high carbon working capacity. Additionally, toluene is widely used as an industrial solvent, in paper-coating operations, for instance. Thus, toluene was selected for a preliminary pure component VOC study.

Air saturated at 23°C with toluene was flowed through the 0.9-cm-diameter column packed with 7.47 g GAC. Three regenerations were run at the conditions given below.

Cycle	Loading & Residual	Regeneration Conditions
1	loading: 1.78 g; 0.238 g/g carbon	T = 24°C Liquid CO_2 P = 1300 psi 150 SL @ 10 SL/min
	residual: 0.07 g/ 0 g/g	
2	loading: 1.64 g; 0.220 g/g	T = 24°C Gaseous CO_2 P = 500 psi 101 SL @ 10 SL/min
	residual: 1.66 g; 0.222 g/g	
3	loading: 1.66 g; 0.222 g/g	T = 24°C Liquid P = 1200 psi 138 SL @ 10 SL/min
	residual: 0.22 g; 0.029 g/g	

The first and third regenerations with liquid CO_2 were effective in removing toluene from the GAC. The gaseous CO_2 was totally ineffective for desorbing toluene.

The following grid generalizes these toluene results and those for the gasoline vapor desorptions:

Fluid	State	Hydrocarbon Desorption from Activated Carbon
CO_2	gaseous T = 24°C P = 500 psi	totally ineffective
CO_2, Freon 13	near critical T = 24°C	very good
CO_2, Freon 13	supercritical T = 50°C	excellent

Thus, preliminary results indicated that CO_2 and Freon in the near-critical or supercritical states were effective in regenerating activated carbon loaded with hydrocarbons; while gaseous CO_2 was totally ineffective.

2. Process Studies with Gasoline

Additional experiments were done to determine what conditions of temperature and pressure were suitable to use as regeneration conditions for the multicycle adsorption/regeneration cycles. Four of the seven-gram capacity columns, packed with the BPL 12x30 mesh GAC, were loaded with BP 89-octane no-lead gasoline vapors. Loading was allowed to continue until column effluent hydrocarbon concentration was 80 percent of that in the column influent. The columns were then regenerated with supercritical carbon dioxide at different conditions.

	Regeneration Conditions	
	Pressure	Temperature
Column 1	103 atm	25°C
Column 2	103 atm	50°C
Column 3	207 atm	50°C
Column 4	207 atm	25°C

Approximately 180 SL of CO_2 were used for each regeneration; the flow rate was 15 SL/min. Three adsorption/regeneration cycles were run; the results are tabulated in Table VII.3. After cycle one, columns one and four had residuals of 0.05 g, whereas columns two and three had residuals of -0.01 and -0.04 g, respectively. The negative residuals suggest that the virgin carbon was initially slightly contaminated with

TABLE VII.3

Three Cycle Adsorption/Regeneration

Carbon = Calgon BPL 12 x 30 Mesh
Gasoline = B.P. no-lead 87 octane
Adsorption column influent flow rate = 180 ml/min
Adsorption termination when effluent hydrocarbon concentration = 80% of influent concentration
Desorption CO_2 flow rate = 15 SL/min
Desorption CO_2 volume = 180 SL

Column	Weight Carbon	Gasoline Loading 1	(g/g)	Regeneration Pressure/Temperature	Residual After Regeneration 1
1	7.41 g	1.80 g	0.243	1500 psi/25°C	0.05 g
2	7.66	1.93	0.252	1500/50	-0.01
3	7.39	1.86	0.252	3000/50	-0.04
4	7.20	1.76	0.244	3000/25	0.05

Column	Gasoline Loading 2	(g/g)	Regeneration Pressure/Temperature	Residual After Regeneration 2
1	1.86 g	0.251	1500 psi/25°C	0.07 g
2	1.97	0.257	1500/50	-0.01
3	1.86	0.252	3000/50	-0.03
4	1.81	0.251	3000/25	0.07

Column	Gasoline Loading 3	(g/g)	Regeneration Pressure/Temperature	Residual After Regeneration 3
1	1.88 g	0.254	1500 psi/25°C	0.11 g
2	1.91	0.249	1500/50	0.03
3	1.82	0.246	3000/50	0.02
4	1.80	0.250	3000/25	0.06

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volatile species, or that the water loading baseline varied slightly. After cycle two, columns one and four had residuals of 0.07 g, and columns two and three had residuals of -0.01 and -0.03 g, respectively. After the third cycle, columns one and four had residuals of 0.11 and 0.06 g, respectively, and columns two and three had residuals of 0.03 and 0.02 g, respectively.

These date indicate that over three cycles, regenerations run at 207 atm are not significantly different than those run at 103 atm, and regenerations run at 50°C are more complete than those run at 25°C.

Based on these results, regeneration conditions of P = 103 atm and T = 50°C were selected for the multicycle adsorption/regeneration experiments.

3. Process Studies with Industrial VOC's

After the selection of ethanol (EtOH) and methyl ethyl ketone (MEK) as the two industrial volatile organic compounds (IVOC's) for study, preliminary experiments were done to show that GAC loaded with these compounds could be regenerated by liquid CO_2. The procedure employed in the gasoline adsorption/regeneration cycles was used.

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Air saturated with the VOC at 24°C was flowed at approximately 800 cc/min through a 1.7-cm diameter, 16-cm long high-pressure pipe packed with 15.46 g of Calgon 12x30 mesh BPL carbon. The adsorptions were not terminated at a particular breakthrough point, but rather at 30 minutes of adsorption time for the MEK, or at 60 minutes for the EtOH. Regenerations were run immediately after adsorption, with the column open to the atmosphere when it was being transferred between the adsorption and regeneration equipment; the humidity of the VOC carrier air was not controlled.

The MEK was Union Carbide commercial grade (99+%) from a 55 gal drum; the EtOH was Publicker Industries Company 200 proof "Pharmco" brand.

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The carbon loadings, regeneration conditions and residual weights for each cycle are presented in Table VII.4.

T. VII.4

All four regenerations were run with liquid CO_2 at 109 atm. In each cycle, the VOC was completely removed from the column; over four cycles there was no indication of residual build-up. The working capacity at 24°C of 0.21 g MEK/g carbon was approximately 80% of the capacity for no-lead gasoline vapors (0.26 g BP 89-octane no-lead/g carbon); the 0.16 g EtOH/g carbon working capacity was about 60% of the capacity for the no-lead gasoline vapors. Thus, preliminary studies indicated that liquid CO_2 was very effective as a regenerant for GAC loaded with MEK or EtOH.

Process studies and multicycle regenerations were run using at least 100 standard liters of CO_2 for the eight-gram carbon bed (about 22.5 lbs of CO_2 per lb GAC). Because it is desirable to operate with minimum solvent usage, two tests were run with MEK at lower CO_2 usages to determine if lesser quantities would give adequate regeneration. The results are summarized in Table VII.5. As can be seen, 14 standard liters (3.4 lbs of CO_2 per lb GAC) gave essentially the same capacity recovery as the larger CO_2 volumes.

T. VII.5

4. Multicycle Tests

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Multiple cycle adsorption/regenerations were run on a 0.9-cm-diameter by 23.5-cm-long column packed with Calgon BPL 12x30 mesh GAC. Equilibrium vapor of a British Petroleum 89-octane unleaded gasoline in air was loaded at 200 cc/min onto the GAC column; the loading was terminated when the hydrocarbon content of the column effluent reached 80% of the column influent, as determined with the FID after loading, the column was regenerated with CO_2 at 103 atm and about 50°C; approximately 100 SL of CO_2 were used at a flow rate of 15-20 SL/min. After regeneration, constant humidity air was flowed through the column at a flow rate of 2.5 L/min for about 1 minute to desorb residual CO_2.

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TABLE VII.4

FOUR-CYCLE ADSORPTION/REGENERATION

Carbon = 15.46 g Calgon BPL 12x30 Mesh

Cycle	VOC	Loading and Residual			Regeneration Conditions*
1	MEK	Loading 3.28g	0.212	g/g carbon	T = 23°C Liquid CO_2
					P = 1600 psi
		Residual-0.05g	0	g/g	127 SL @ 10 SL/min
2	MEK	Loading 3.33g	0.215	g/g	T = 25°C
					P = 1600 psi Liquid CO_2
		Residual-0.05g	0	g/g	137 SL @ 10 SL/min
3	EtOH	Loading 2.43g	0.157	g/g	T = 24°C
					P = 1600 psi Liquid CO_2
		Residual-0.09 g	0	g/g	124 SL @ 20 SL/min
4	EtOH	Loading 2.44g	0.158	g/g	T = 24°C
					P = 1600 psi Liquid CO_2
		Residual-0.06g	0	g/g	122 SL @ 20 SL/min

*For all regenerations, the last approximately 30 SL are $P_{sat} \approx$ 900 psi.

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TABLE VII.5

REDUCED CO_2 USAGE REGENERATION TESTS

Mass carbon (Calgon BPL 12x30 Mesh): 7.56g
Mass carbon and column : 435.57g

Column Loaded with Equilibrium MEK vapor in air at 23°C (∿ 1 x 10^5 ppmv)

Regeneration Conditions: T = 50°C
P = 1500 psia

	After MEK Loading				After Regeneration		
Cycle	Column Mass	MEK Mass	g/g carbon	SL CO_2	Column Mass	MEK Residual	Residual g/g carbon
1	438.41g	2.84g	0.376	20	435.83g	0.26g	0.034
2	438.35	2.78	0.368	14	436.06	0.49	0.065

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The results for 25 adsorption/regeneration cycles for unleaded gasoline are tabulated in Table VII.6. The initial mass of the column and the virgin GAC (equilibrated with constant humidity air) was 435.42 g. After 25 cycles, the mass was 435.42 g, i.e., the carbon was 100% regenerated. The working capacity of the carbon was 0.24 g/g carbon; using as little as 89 SL of CO_2 appeared to completely regenerate the carbon.

Another series of multiple cycle adsorption/regenerations were run using British Petroleum 89-octane leaded gasoline. The same adsorption procedures as in work with the unleaded gasoline were employed. The air/leaded gasoline stream had a smaller flow rate: about 150 cc/minute vs 200 cc/minute for unleaded. Similar regeneration conditions were used to desorb the leaded gasoline as in the unleaded case.

The results of 25 adsorption/regeneration cycles for leaded gasoline are tabulated in Table VII.7. The initial mass of the column and the virgin GAC was 436.30 g. After 25 cycles, the mass was 436.28 g, i.e., the carbon was 100% regenerated (the experimental precision is ± 0.02 g). There were gasoline residuals on the carbon after regenerations 6 and 11; cycles 6 and 11 had relatively high initial gasoline loadings, 0.249 g/g and 0.254 g/g, respectively. The working capacity of the carbon 0.25g/g carbon. After the twenty-fifth regeneration, the column was saved for future work with the IVOC's.

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After the 25th cycle of the leaded gasoline vapor testing, additional adsorption/regeneration cycles were carried out with ethanol vapor. Equilibrium vapor of 200 proof ethanol in air, about 6×10^4 vol. ppm at 23°C, was flowed at 1.5 SL/min through the GAC column. The loading was terminated when the ethanol content of the column effluent reached 80% of the column influent, as determined with the FID. After loading, the column was regenerated with CO_2 at 103 atm, and temperatures slightly lower than used for the gasoline vapor regeneration, 41 to 51°C. The results for 25 adsorption/regeneration cycles are tabulated in Table VII.8.

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TABLE VII.6

25-CYCLE ADSORPTION/REGENERATION TEST

Mass carbon (Calgon BPL 12 x 30 Mesh): 8.06 g
Mass carbon and column : 435.42 g

Column loaded with equilibrium gasoline vapor (British Petroleum 87 octane, no-lead) at 23°C

Regeneration conditions: CO_2 at 1350 ≤ P ≤ 1550 psig
flow rate = 15-20 SL/min

Cycle	After gasoline loading: Column Mass	Gasoline Mass	g/g carbon	After regeneration: Regeneration Volume CO_2	T ±2°C	Column Mass
0	435.42 g					
1	437.36 g	1.94 g	0.241	107 SL	53°C	435.41 g
2	437.33	1.91	0.237	104	54	435.42
3	437.35	1.93	0.239	106	54	435.41
4	437.33	1.91	0.237	105	54	435.41
5	437.36	1.94	0.241	113	54	435.41
6	437.33	1.91	0.237	111	54	435.39
7	435.37	1.95	0.242	112	52	435.42
8	437.33	1.91	0.237	89	54	435.41
9	437.38	1.96	0.243	100	52	435.42
10	437.36	1.94	0.241	103	54	435.41
11	436.97	1.55	0.192	118	54	435.38
12	437.34	1.92	0.238	113	54	435.42
13	437.36	1.94	0.241	93	54	435.40
14	437.32	1.90	0.236	114	53	435.42
15	437.38	1.96	0.243	102	54	435.42
16	437.40	1.98	0.246	93	51	435.42
17	437.37	1.95	0.242	97	54	435.42
18	437.41	1.99	0.247	98	49	435.40
19	437.36	1.94	0.241	99	54	435.40
20	437.35	1.93	0.239	97	54	435.41
21	437.40	1.98	0.246	102	54	435.41
22	437.33	1.91	0.237	101	54	435.42
23	437.36	1.94	0.241	102	54	435.41
24	437.39	1.97	0.244	105	54	435.42
25	437.39	1.97	0.244	103	54	435.42

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TABLE VII.7

GASOLINE VAPOR ADSORPTION ON GAC;
25-Cycle Test with Supercritical Carbon Dioxide Regeneration

Mass carbon (Calgon BPL 12 x 30 Mesh): 8.24 g
Mass carbon and column : 436.30 g

Column loaded with equilibrium gasoline vapor (British Petroleum 89 octane, leaded) at 23°C

Regeneration conditions: CO_2 at $1350 \leq P \leq 1550$ psig
flow rate = 13-17 SL/min

	After gasoline loading:			After regeneration:		
Cycle	Column Mass	Gasoline Mass	g/g carbon	Regeneration Volume CO_2	T ±2°C	Column Mass
0	436.30 g					
1	438.33 g	2.03 g	0.246	105 SL	52°C	436.32 g
2	438.35	2.05	0.249	109	53	436.30
3	438.35	2.05	0.249	120	53	436.29
4	438.34	2.04	0.248	107	53	436.30
5	438.37	2.07	0.251	112	54	436.29
6	438.35	2.05	0.249	117	52	436.35
7	438.40	2.10	0.255	111	52	436.32
8	438.36	2.06	0.250	107	52	436.30
9	438.34	2.05	0.249	112	52	436.30
10	438.37	2.07	0.251	105	52	436.30
11	438.39	2.09	0.254	109	52	436.34
12	438.33	2.03	0.246	114	52	436.31
13	438.36	2.06	0.250	120	52	436.31
14	438.26	1.96	0.238	119	52	436.29
15	438.24	1.94	0.235	116	52	436.28
16	438.26	1.96	0.238	112	52	436.30
17	438.27	1.97	0.239	114	52	436.29
18	438.25	1.95	0.237	116	52	436.28
19	438.26	1.96	0.238	115	52	436.29
20	438.25	1.95	0.237	115	52	436.28
21	438.22	1.92	0.233	123	52	436.28
22	438.35	2.05	0.249	116	52	436.28
23	438.24	1.94	0.235	116	52	436.28
24	438.25	1.95	0.237	115	52	436.29
25	438.26	1.96	0.238	118	52	436.28

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TABLE VII.8

TWENTY FIVE-CYCLE ETHANOL (ADSORBATE)/CO_2 (REGENERANT) TEST; GAC HAS HAD 25 PREVIOUS CYCLES WITH LEADED GASOLINE ADSORBATE

Mass carbon (Calgon BPL 12 x 30 Mesh): 8.24 g
Mass carbon and column : 436.30 g

Column loaded with equilibrium ethanol vapor at 23°C (Publicker Industries, Co., 200 proof; ~6×10^4 vol.ppm)

Regeneration conditions: CO_2 at $1350 \leq p \leq 1550$ psig
flow rate 13-17 SL/min

	After EtOH loading:			After regeneration:		
Cycle	Column Mass	EtOH Mass	g/g carbon	Regeneration Volume CO_2	T ±2°C	Column Mass
(0)	436.30 g					
1(26)	439.03 g	2.73 g	0.331	117 SL	41°C	436.30 g
2(27)	438.85	2.55	0.309	115	44	436.29
3(28)	438.88	2.58	0.313	116	48	436.30
4(29)	438.91	2.61	0.317	105	48	436.30
5(30)	438.90	2.60	0.316	104	48	436.30
6(31)	438.91	2.61	0.317	109	48	436.29
7(32)	438.93	2.63	0.319	106	49	436.29
8(33)	438.85	2.55	0.309	110	50	436.29
9(34)	438.94	2.64	0.320	108	50	436.29
10(35)	438.81	2.51	0.305	109	48	436.29
11(36)	438.88	2.58	0.313	109	51	436.29
12(37)	438.85	2.55	0.309	106	50	436.29
13(38)	438.95	2.65	0.322	105	48	436.29
14(39)	438.88	2.58	0.313	106	47	436.30
15(40)	438.89	2.59	0.314	109	48	436.29
16(41)	438.91	2.61	0.317	107	49	436.29
17(42)	438.89	2.59	0.314	109	48	436.28
18(43)	438.86	2.56	0.311	106	49	436.29
19(44)	438.85	2.55	0.309	111	48	436.30
20(45)	438.90	2.60	0.316	107	51	436.29
21(46)	438.87	2.57	0.312	107	49	436.29
22(47)	438.87	2.57	0.312	106	50	436.29
23(48)	438.95	2.65	0.322	107	48	436.29
24(49)	439.00	2.70	0.328	109	51	436.29
25(50)	438.85	2.55	0.309	106	50	436.30

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The carbon was 100% regenerated after each cycle; the working capacity was about 0.32 g/g.

Thus, after 50 adsorption/regeneration cycles, 25 cycles with leaded gasoline vapor adsorbate and 25 cycles with ethanol vapor adsorbate, the carbon retained 100% of its virgin working capacity.

Further testing on this carbon bed included multicycle tests with methyl ethyl ketone. Equilibrium vapor of Doe and Ingalls Industries Co. industrial grade methyl ethyl ketone in air, about 1.13×10^5 vol. ppm at 22°C, was flowed at 0.8 SL/min through the GAC column. The loading was terminated when the MEK content of the column effluent reached about 80% of the column influent. After loading, the column was regenerated with CO_2 at 103 atm, and temperatures of 40-64°C.

The results for the 25 adsorption/regeneration cycles are tabulated in Table VII.9. A residual of 0.02 g, which could not be removed with up to 235 SL of CO_2 (at 50°C and 103 atm), was left on the carbon. After the first four cycles, it was discovered that the MEK had attacked the rubber gaskets in the flowmeter upstream of the carbon bed; some of the rubber was probably adsorbed on the carbon and caused its 0.02 g increase in mass.

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While 100-110 of CO_2 at 50°C and 103 atm could completely regenerate carbon loaded with gasoline vapors or EtOH, approximately 150 SL of CO_2 were necessary to regenerate the MEK-loaded carbon. With 120 SL of CO_2 regeneration, or about a 0.07 g residual, the carbon working capacity was about 0.33 g MEK/g carbon; with 150 SL of regeneration, or a 0.02 g residual, the carbon working capacity was approximately 0.34g MEK/g carbon.

Figure VII.3 shows the working capacity as a function of cycle number over the entire 75-cycle test.

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TABLE VII.9

25-CYCLE METHYL ETHYL KETONE (MEK)(ADSORBATE)/CO_2 (REGENERANT) TEST; GAC HAS HAD 50 PREVIOUS CYCLES WITH LEADED GASOLINE ADSORBATE AND ETHANOL ADSORBATE (25 CYCLES EACH)

Mass carbon (Calgon BPL 12 x 30 Mesh): 8.24 g
Mass carbon and column : 436.30 g

Column loaded with equilibrium MEK vapor at 22°C
(Doe and Ingalls Industries ~1.13×10^5 vol. ppm)

Regeneration Conditions: CO_2 at $1350 \leq p \leq 1550$ psig
flowrate 12-17 SL/min

	After MEK Loading:			After Regeneration:		
Cycle	Column Mass	MEK Mass	g/g carbon	Regeneration Volume CO_2	T ±2°C	Column Mass
(0)	436.30 g					
1(51)	439.14 g	2.84 g	0.345	106 SL	40°C	436.33 g
2(52)	439.18	2.88	0.350	111	48	436.34
3(53)	439.11	2.81	0.341	105	57	436.39
4(54)	439.19	2.89	0.351	115	53	436.37
5(55)	439.21	2.91	0.353	113	50	436.35
6(56)	439.15	2.85	0.346	109	50	436.36
7(57)	439.14	2.84	0.345	137	51	436.34
8(58)	439.13	2.83	0.343	134	49	436.32
9(59)	439.16	2.86	0.347	125	52	436.35
10(60)	439.15	2.85	0.346	140	52	436.33
11(61)	439.16	2.86	0.347	163	52	436.32
12(62)	439.18	2.88	0.350	146	50	436.32
13(63)	439.12	2.82	0.342	96	49	436.37
14(64)	439.16	2.86	0.347	146	49	436.33
15(65)	439.15	2.85	0.346	219	55	436.33
16(66)	439.14	2.84	0.345	163	51	436.32
17(67)	439.13	2.83	0.343	105	49	436.37
18(68)	439.11	2.81	0.341	119	51	436.37
19(69)	439.16	2.86	0.347	204	51	436.33
20(70)	439.16	2.86	0.347	222	50	436.33
21(71)	439.15	2.85	0.346	205	49	436.32
22(72)	439.16	2.86	0.347	205	51	436.32
23(73)	439.16	2.86	0.347	202	52	436.32
24(74)	439.17	2.87	0.348	235	52	436.32
25(75)	439.16	2.86	0.347	119	64	436.38

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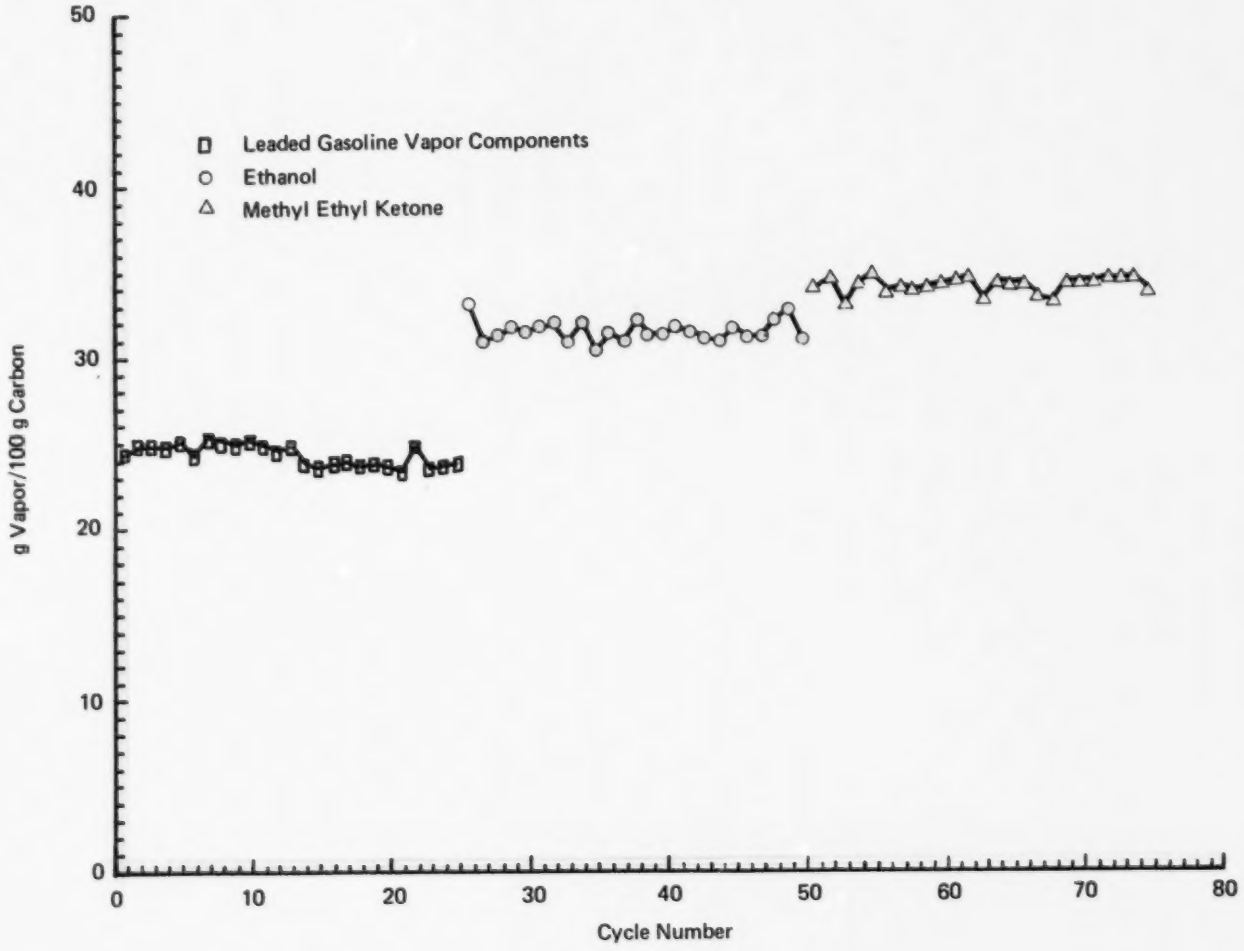

FIGURE VII.3 CARBON WORKING CAPACITY VS. CYCLE NUMBER FOR SEVENTY-FIVE CYCLE TEST WITH SUPERCRITICAL CARBON DIOXIDE REGENERATION

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VIII. ADSORBATE/REGENERANT SEPARATION

The effluent stream from a carbon column undergoing regeneration with a supercritical fluid must have nearly complete separation of the adsorbate from the regenerant so that the regenerant may be recycled. This section discusses separation of CO_2 regenerant from the different test adsorbates: gasoline vapor components, ethanol, and methyl ethyl ketone.

A. CO_2/GASOLINE VAPOR COMPONENT SEPARATION

The feed stream to a CO_2/gasoline vapor component (GVC) separation system would be at typical carbon regeneration temperature and pressure: 100 atm and 50°C. The stream would be between 1 and 10 mole% hydrocarbon in CO_2, most likely at the low end of that range (see Appendix C). The gasoline vapor components would be approximately 50 mole% n-butane, 30 mole% isopentane, 2 mole% n-hexane, with the remainder being light paraffins, olefins and aromatics (C_5-C_8).

Liquid-liquid phase or liquid-solid phase separations for CO_2-GVC separation are first discussed. Following this, a vapor-liquid separation approach is presented in greater detail, as it became apparent that this would be the favored route.

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1. Liquid-Liquid Phase and Liquid-Solid Phase Separation

Figure VIII.1A is a pressure-temperature diagram for the CO_2-n-butane system (Figures VIII.1A and VIII.1B are from Schneider, 1967). The solid lines represent the pure components' sublimation, fusion, and vaporization equilibrium relationships. CP1 and CP2 denote the critical points of CO_2 (73 atm, 31°C) and n-butane (37 atm, 152°C), respectively; the dashed line connecting them is the critical envelope. To the left of the CO_2 fusion curve S_1, and to the right of n-butane fusion curve S_2, a liquid phase can exist in equilibrium with solid CO_2. To the left of the n-butane fusion curve S_2, and to the right of the dashed curve LS_1S_2, three phases

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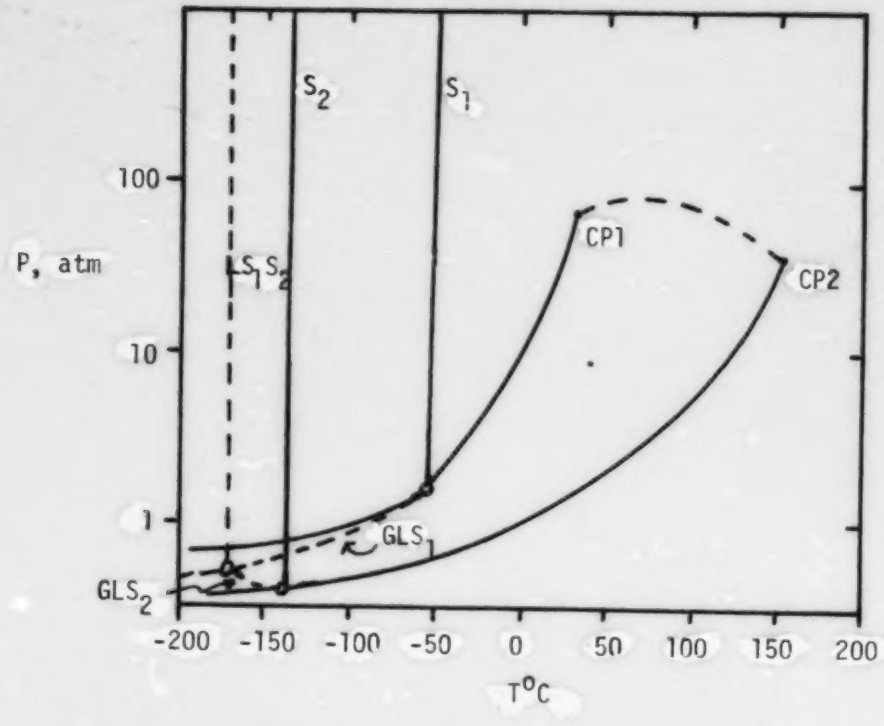

FIGURE VIII.1A: P VS T FOR CO_2 (1) - N-BUTANE (2)

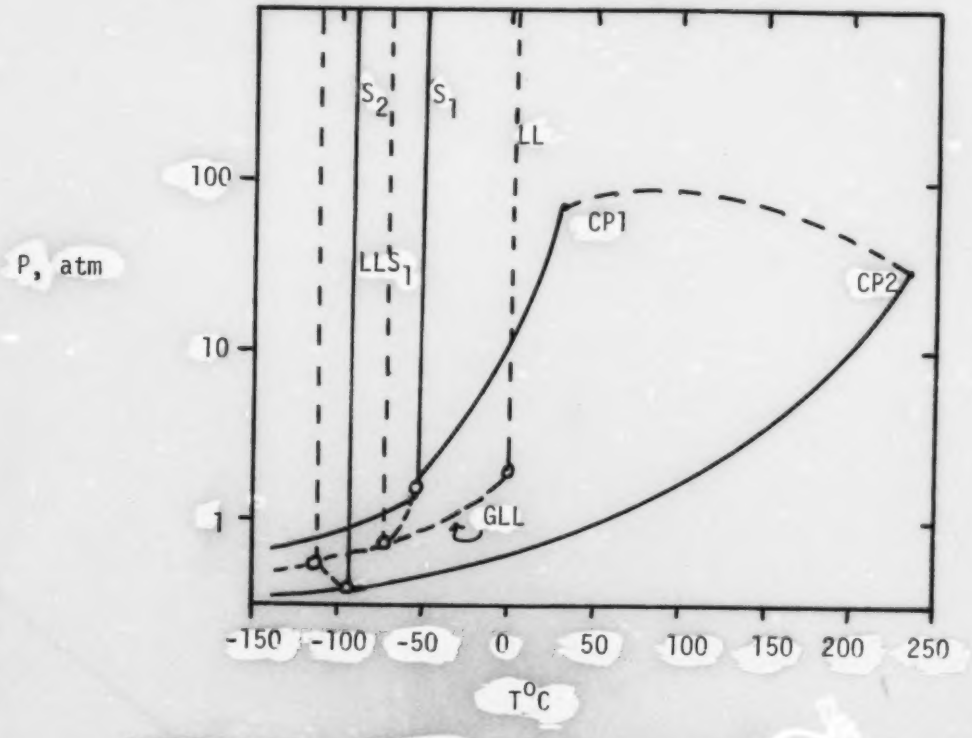

FIGURE VIII.1B: P VS T FOR CO_2 (1) - N-HEXANE (2)

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can coexist: liquid CO_2, solid CO_2, and solid n-butane. To the left of LS_1S_2 exist solid phases of n-butane and CO_2.

The effect a CO_2-n-butane separation at 100 atm, the temperature could be reduced to within the range bounded by S_1 and S_2 (i.e., between -55° and -138°C). If the CO_2 mol fraction were relatively high, the temperature at which this separation occurred would be relatively close to the pure CO_2 fusion temperature, -55°C. In some fashion, the liquid phase could be decanted; if it contained a significant fraction of CO_2, a distillation would be necessary. The solid CO_2 phase would be heated to provide CO_2 recycle.

The mechanical means for separating the liquid phase from the solid for a continuous process would be more complex than that for a batch system; some variety of screw-conveyor would have to be employed to move the solid CO_2 from the freezing region of the separator to the rewarming section.

While the phase behavior of the CO_2-n-pentane system is very similar to that of the CO_2-n-butane system, the CO_2-n-hexane system is more complex. Figure VIII.1B is a pressure-temperature diagram of the CO_2-n-hexane system. As in Figure VIII.1A, the solid lines are the pure components' phase equilibrium relationships; CP_2 is the critical point of n-hexane (30 atm, 235°C). In the region between LL and S_1, two liquid phases exist; between S_1 and LLS, three phases co-exist: solid CO_2 and two liquid phases.

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To effect a CO_2-n-hexane separation at 100 atm, the temperature could be reduced to within the range bounded by LLS and LL. If the temperature was below LL, but greater than -55°C (S_1), the two liquid phases could be separated by virtue of density difference. Distillation of either or both phases might then be necessary to reach the desired purities. If the temperature was above LLS, but less than -55°C, the liquid phases could be decanted from the solid CO_2 and then separated from one another as above.

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It is not known if the phase behavior of the mixture of CO_2 and gasoline vapor components is similar to either the CO_2-n-hexane or CO_2-n-butane systems. We do not have experimental phase-equilibria data for any ternary or higher-order CO_2-hydrocarbon systems. Although the Peng-Robinson equation of state (Peng and Robinson, 1976) can be used to theoretically predict phase equilibria for CO_2-hydrocarbon systems (Peng, et al., 1979; Modell, et al., 1979) the procedure is straightforward only for binary systems. Thus, it appears that experimental phase-equilibria data for gasoline vapor components - CO_2 mixtures are essential if the feasibility of a two-liquid-phase or liquid-solid phase separation scheme is to be evaluated. In the absence of these data, use of these phase separation methods was ruled out.

2. Vapor-Liquid Separation: Distillation

Vapor-liquid equilibrium data for the CO_2-n-butane system at 34 atm* (Olds, et al., 1949; Poettman and Katz, 1945) are plotted in Figure VIII.2.

To achieve a separation with,

$$X_{CO_2} \text{ bottoms} < 0.01$$

$$X_{CO_2} \text{ distillate} > 0.99$$

a graphical calculation using the McCabe-Thiele method indicates that the minimum number of theoretical stages equals seven.

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A column design with a low reflux ratio is feasible because of the high CO_2 feed concentration ($X_{CO_2} \geq 0.9$) and high relative CO_2/n-butane volatility. The feed stream at 100 atm and 50°C is flashed to 34 atm, and in so doing is about 75% vaporized, if the mixture thermodynamic properties are assumed to be equal to those of pure CO_2. Assuming D/V (= total overhead product rate/CO_2 phase rate) = 0.6, or L/V (= slope

*Slightly below the maximum pressure at which complete CO_2-n-butane separation can be effected -- 37 atm, the critical pressure of n-butane.

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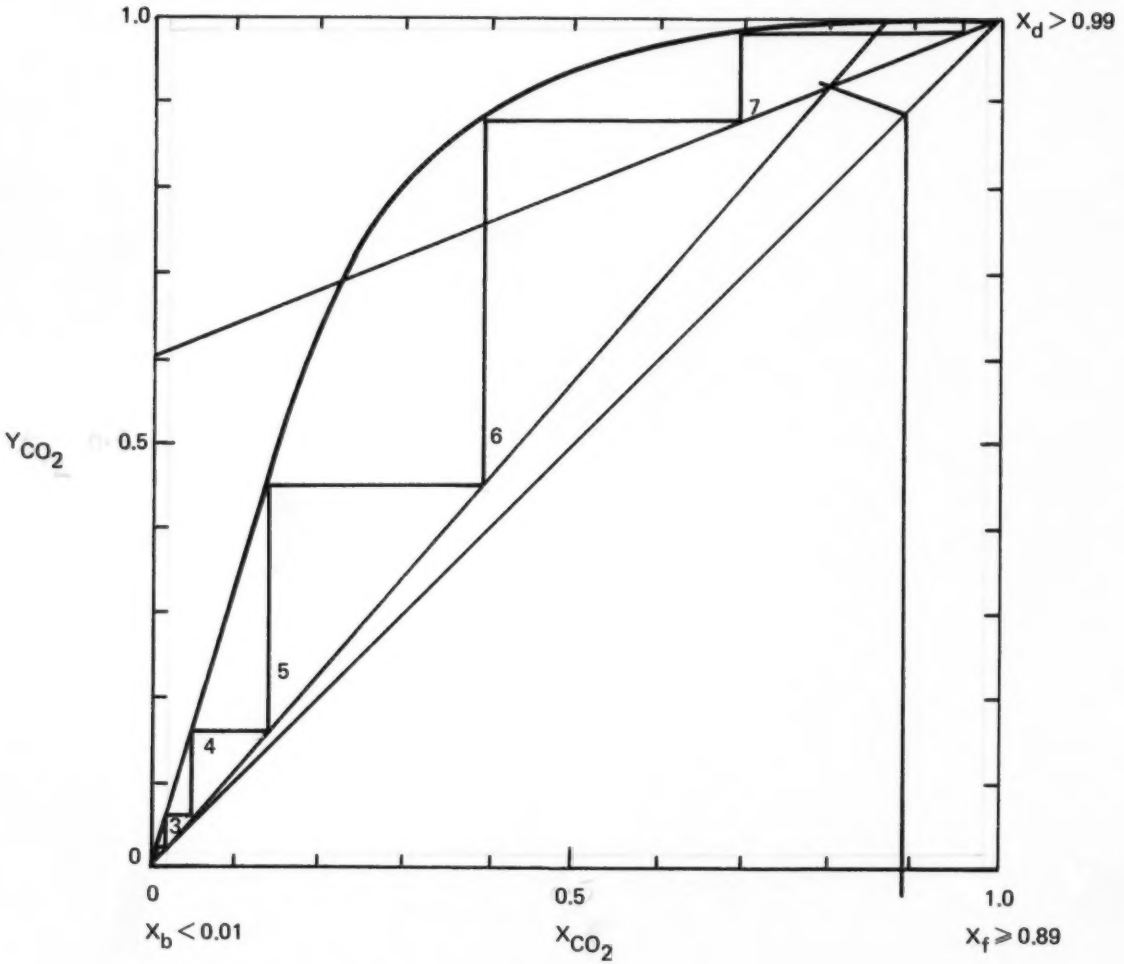

FIGURE VIII.2 MCCABE-THIELE PLOT FOR CO_2-n-BUTANE AT 34 ATM

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of upper operating line) = 0.4 when Y_{CO_2} distillate $\simeq$ 1.0, nine theoretical stages can be stepped off on Figure VIII.2. The external reflux ratio at the top of the column is 0.67.

The column has the feed introduced between the seventh and eighth stages and has a partial condenser. The distillate (vapor at 0°C and 34 atm) is compressed to 100 atm and 50°C in a two-stage compressor. Figure VIII.3 is a flowsheet for this distillation system.

F VIII.3

The column design cannot be optimized with respect to reflux ratio versus total number of stages (column height) until the height equivalent to a theoretical plate (HETP) is known. The HETP is preferably obtained by experiment, although there are correlations in the literature (e.g., Murch, 1953), which may be used for preliminary design estimates. One would expect low mass transfer resistances between the liquid and vapor phases at the temperatures and pressure under consideration, and hence relatively small HETP's.

The energy requirements of the sample nine-stage system depicted in Figure VIII.3 are estimated as follows:

Work requirement at column top

Heat absorption by partial condenser

= ΔH_{vap} CO_2 at 34 atm (0°C) = 101 Btu/lb L
= 4445 Btu/lb mol L
= 2620 Btu/lb mol feed

C.O.P. (coefficient of performance) = $\frac{\text{refrigeration obtained}}{\text{work required}}$

to provide cooling at 0°C (273K)
reject heat at 30°C (303K)

$$\text{C.O.P.} = \frac{273}{(303-273)} = 9.1$$

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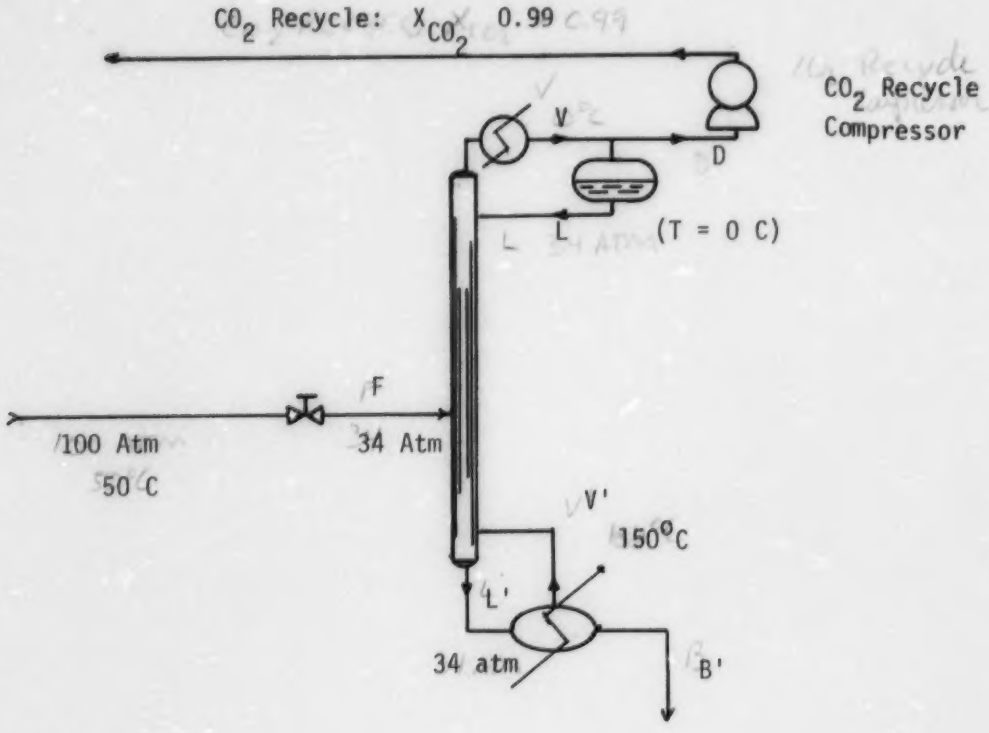
FIGURE VIII.3

CO_2-Butane Separation Flow Sheet



D/V = 0.6

L/V = 0.4

L'/V' = 1.15

D = 0.89 F mols

B = 0.11 F mols

V = 1.48 F mols

L = 0.59 F mols

V' = 0.73 F

L' = 0.84 F

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$$\text{Work} = \frac{\text{heat adsorbed}}{(\text{C.O.P.})(\text{mechanical efficiency})} = \frac{2623}{(9.1)(0.65)} = 440 \text{ Btu/lb mol feed}$$

Energy requirement at reboiler

ΔH_{vap} n-butane 150°C = 2340 Btu/lb mol L'
= 1960 Btu/lb mol feed

Energy requirement at recycle compressor

Two-stage isentropic compression

1st stage: 0°C, 34 atm to 40°C, 60 atm

$\Delta H_{isenthalpic}$ = 395 Btu/lb mol D

Assume efficiency of 0.65

W = 610 Btu/lb mol D

2nd stage: 30°C, 60 atm to 70°C, 100 atm

$\Delta H_{isenthalpic}$ = 395 Btu/lb mol D

W = 610 Btu/lb mol D

W total = 1220 Btu/lb mol D
= 1090 Btu/lb mol feed

Total energy requirement (steam source basis)

(440 + 1090) x (0.8/0.34) + 395 = 3995 Btu/lb mol Feed

This assumes the compressor and cooler are run electrically and the reboiler is steam heated; the conversion factor between electrical and steam energy is 0.8/0.34.

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Alternatively, a vapor-recompression distillation system may be used in order to achieve a more energy-efficient CO_2-butane separation. A flowsheet for this system is shown in Figure VIII.4. In this scheme, the entire overhead vapor stream V is fed to compressor C1 where it is compressed to the recycle pressure (100 atm). A portion of the heat of compression of compressor discharge stream 1 is used to heat stream L' in partial reboiler PRB1. The compression ratio, compressor efficiency, and heat exchanger flow rates and efficiency determine the maximum temperature which can be obtained in the reboiler. If this reboiler temperature is insufficient to achieve the desired bottoms purity, stream B would then

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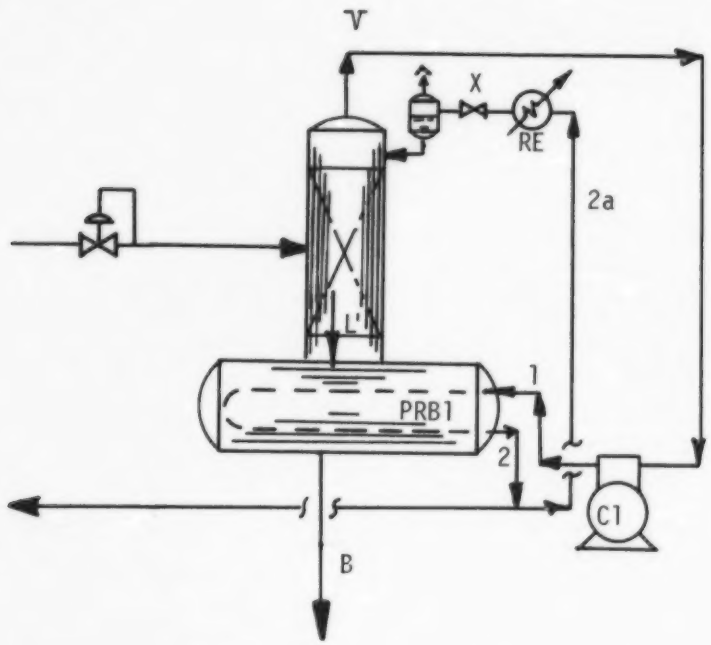
FIGURE VIII.4

Vapor-Recompression Distillation for CO_2-Butane Separation



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have to be flashed to a lower pressure and fed to another separation system.

Reflux at the top of the column is provided by splitting stream 2, cooling split-stream 2a in reflux exchanger RE and flashing back to column pressure by means of valve X. For instance, if stream 2 were at 100 atm and 50°C, 2a could be cooled to about 30°C with cooling water in RE, and upon flashing to 34 atm, would be about 70% liquefied.

The recycle compressor cost would likely be a sizable fraction of the fixed capital investment for this vapor-recompression system, and thus an optimal design would tend towards a relatively small reflux ratio and more theoretical stages.

B. CO_2/IVOC SEPARATION

To carry out the design calculations for a system for removal and recovery of methyl ethyl ketone (MEK) or ethanol, performance of vapor-liquid separations for the binaries CO_2/MEK and CO_2/ethanol are required. As described below in Section IX, detailed calculations were done for an MEK adsorption/regeneration process. In this section, the bases for the CO_2/MEK separation design are given, plus the fundamental information needed for a CO_2/ethanol vapor-liquid separation design.

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No experimental data for the CO_2/MEK system are available, and only fragmentary information has been published for CO_2/ethanol. Thus, two-component phase-equilibrium relationships had to be used to predict the required data from thermodynamic properties of the pure components. A common method, the Lewis and Randall rule (Smith, 1963), was tried, but failed to give reasonable agreement with the published CO_2/ethanol data.

The Peng-Robinson modification of the Redlich-Kwong equation of state has been shown recently to predict vapor-liquid equilibria successfully near the critical point. This approach was tried for both CO_2/ethanol

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and CO_2/MEK, and it was found to adequately model the known CO_2/ethanol data. Thus, it was used for the CO_2/MEK predictions, and the results are shown in Table VIII.1 and Figure VIII.5. Table VIII.2 and Figure VIII.6 show the predictions for CO_2/ethanol. Calculations for CO_2/MEK were done at both 800 psia and 300 psia, in preparation for the design case described below in Section IX.

The CO_2/MEK vapor-liquid equilibrium data were then used to fix the separation system design. The results of that design are summarized in Appendix B. The results show that:

(a) for a feed composition (desorber effluent) of 0.95 CO_2 mol fraction (0.05 MEK mol fraction), at a pressure of 102 atm (1500 psia) and a temperature of 50°C (122°F), a CO_2 purity of 0.999995 can be achieved at a distillation pressure of 54.4 atm (800 psia), representing 90.6 mol% of the feed. The bottoms composition is 0.49 CO_2 mol fraction. Five rectifying stages and one stripping stage are needed, and the reflux ratio is 0.06.

(b) For a feed composition of 0.49 CO_2 mol fraction, at 54.4 atm (800 psia) and 50°C (122°F), an overhead product of 0.991 CO_2 mol fraction is obtained at 20.4 atm (300 psia), representing 38 mol% of the feed. The bottoms composition is 0.18 CO_2 mol fraction. Two stripping stages are needed, with no reflux requirement.

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TABLE VIII.1

VAPOR-LIQUID EQUILIBRIUM DATA FOR CO_2-MEK SYSTEM PREDICTED WITH PENG-ROBINSON EQUATION OF STATE

Interaction Parameter δ = 0.1

p = 800 PSIA	T (^oK)	X_{CO_2}	Y_{CO_2}
	300	0.83	0.994
	310	0.60	0.990
	320	0.50	0.985
	340	0.39	0.975
	360	0.32	0.95
	380	0.28	0.93
	420	0.22	0.82

p = 300 PSIA	T (^oK)	X_{CO_2}	Y_{CO_2}
	278	0.37	0.997
	283	0.33	0.996
	289	0.29	0.995
	300	0.24	0.991
	320	0.18	0.98
	340	0.15	0.96
	360	0.12	0.93
	420	0.067	0.66

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FIGURE VIII.5

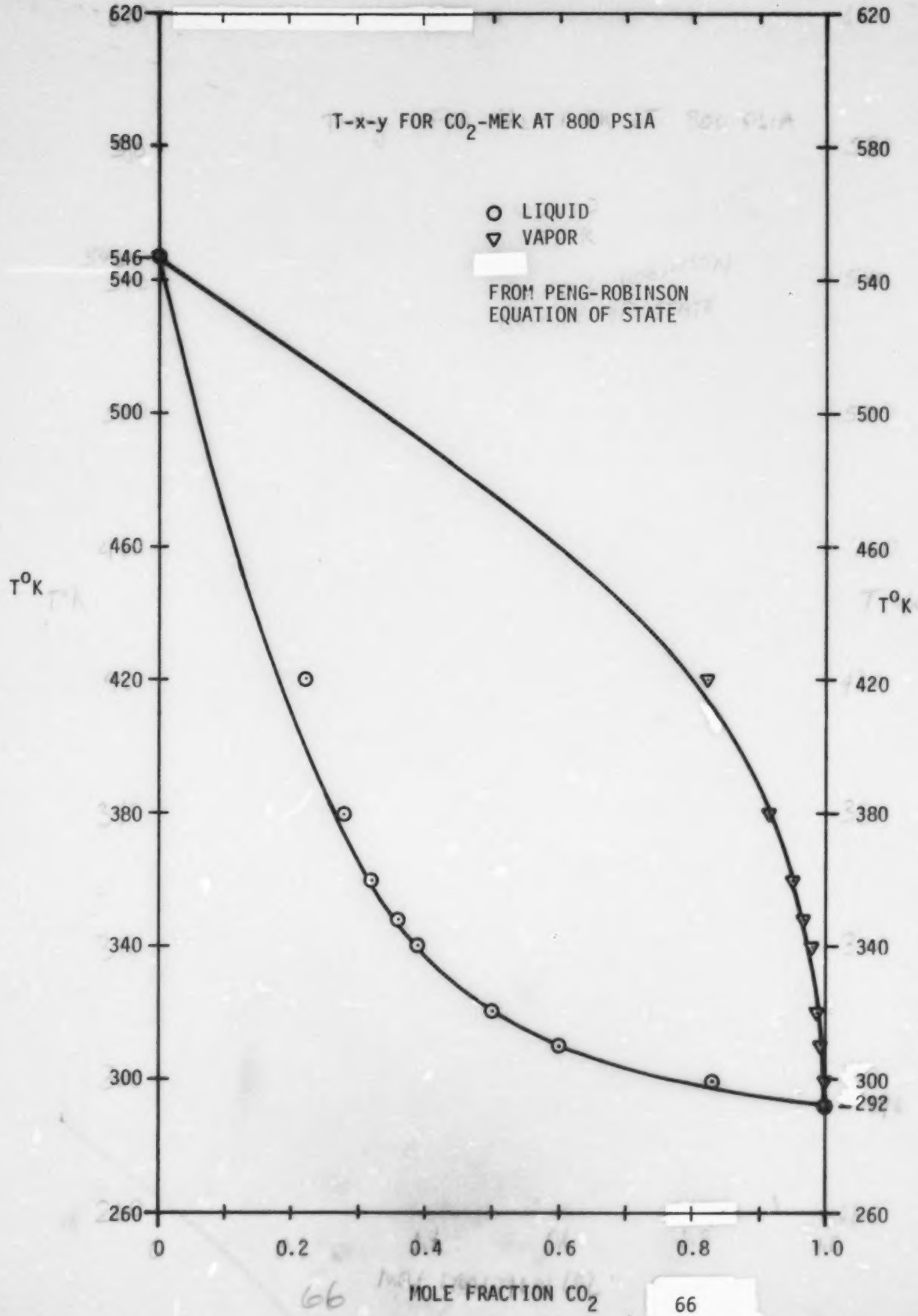

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TABLE VIII.2

VAPOR-LIQUID EQUILIBRIUM DATA FOR CO_2-EtOH SYSTEM PREDICTED WITH PENG-ROBINSON EQUATION OF STATE

Interaction Parameter $\delta_{12} = 0.1$

p = 800 PSIA	T (^oK)	X_{CO_2}	Y_{CO_2}
	298	0.47	0.995
	300	0.44	0.995
	310	0.35	0.992
	320	0.30	0.988
	340	0.24	0.976
	360	0.20	0.952

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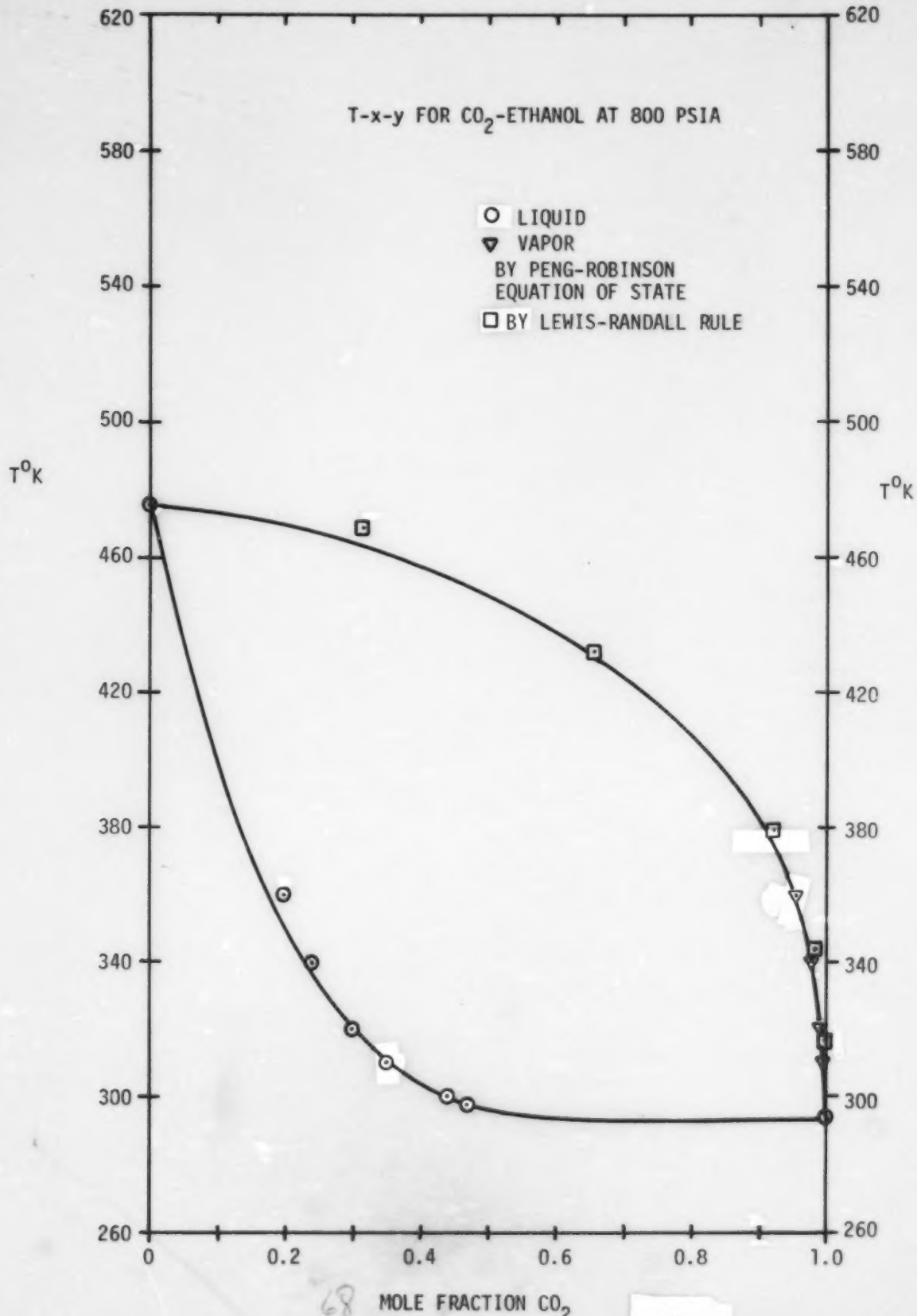
FIGURE VIII.6



IX. PROCESS DESIGN

In this section, the process design of a full-scale system to treat 10,000 scfm of air with 4500 ppmv methyl ethyl ketone vapors is described. The operation of the system is described first; the design of important components, such as adsorption and desorption vessels, is then presented, followed by the capital and operating costs for the system.

A. SYSTEM OPERATION

The adsorption/desorption system described herein is based on the use of supercritical carbon dioxide to remove adsorbed MEK vapors from GAC. The adsorption and desorption vessels are separate because of significant differences in design criteria; thus, the carbon is transported from one to the other. The desorption cycle includes separation of MEK dissolved in the CO_2 effluent by distillation and flash units at several pressure levels, to minimize the loss of CO_2, to recover the maximum amount of MEK adsorbate, and to maximize the purity of CO_2 return to the desorption vessel.

The adsorption cycle operation is depicted schematically in Figures IX.1A-D. The two carbon adsorption vessels CA1 and CA2 and ancillary carbon hoppers H1-H4 are connected to the carbon regeneration vessel CRV and hoppers H5 and H6 via the tubular conveyor TC. The MEK-containing air stream, flowing at 10,000 SCFM with a head of 8" of water, is alternately cycled over a 15-minute adsorption period between CA1 and CA2.

Figure IX.1A depicts a ten-minute phase in the adsorption cycle. Air flows through carbon bed CA1, regenerated carbon from H6 is transferred by TC to H1 and MEK-loaded carbon in H4, previously in CA2, is moved in TC to H5. At the end of this 10-minute period, the system is in the state depicted by Figure IX.1B: H1, H3 and CRV contain regenerated carbon. In the next 2-1/2 minutes, CRV is depressurized and the carbon is transferred to H6; the carbon from H3 is moved into CA2. In the following 2-1/2

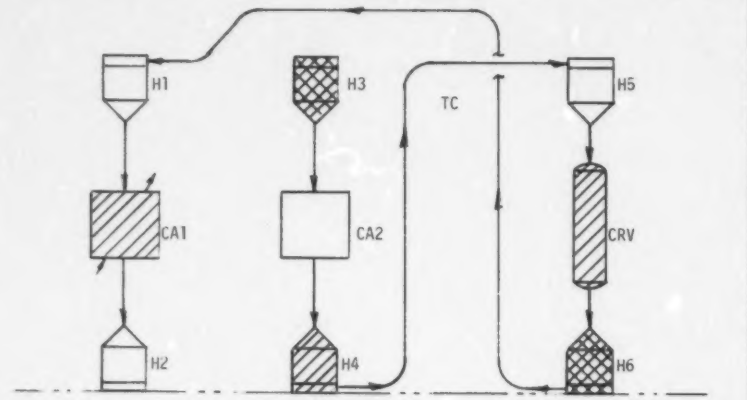


FIGURE IX.1A

Denotes MEK-loaded Carbon

Denotes Regenerated Carbon

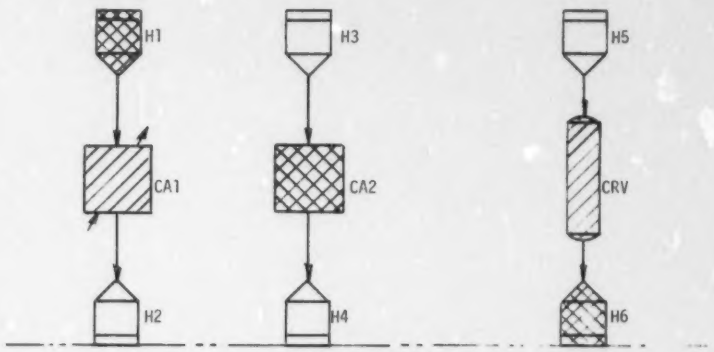


FIGURE IX.1C

Denotes MEK-loaded Carbon

Denotes Regenerated Carbon

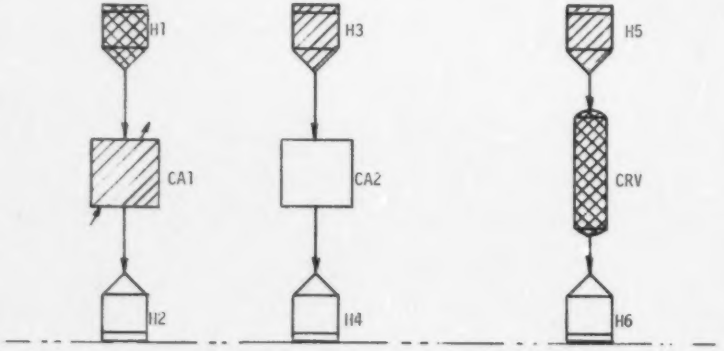


FIGURE IX.1B

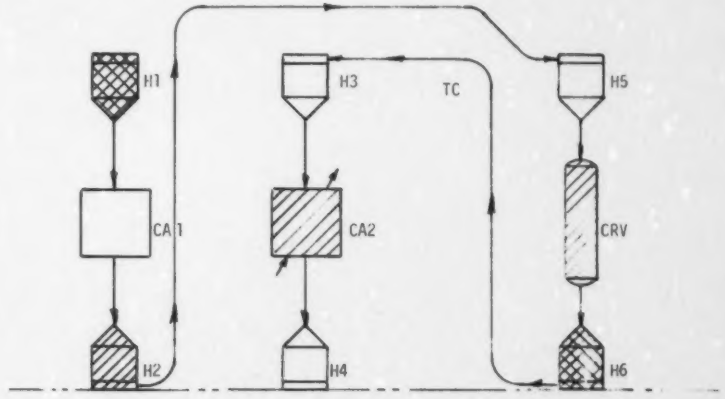


FIGURE IX.1D

FIGURE IX.1: ADSORPTION CYCLE OPERATION SCHEMATIC

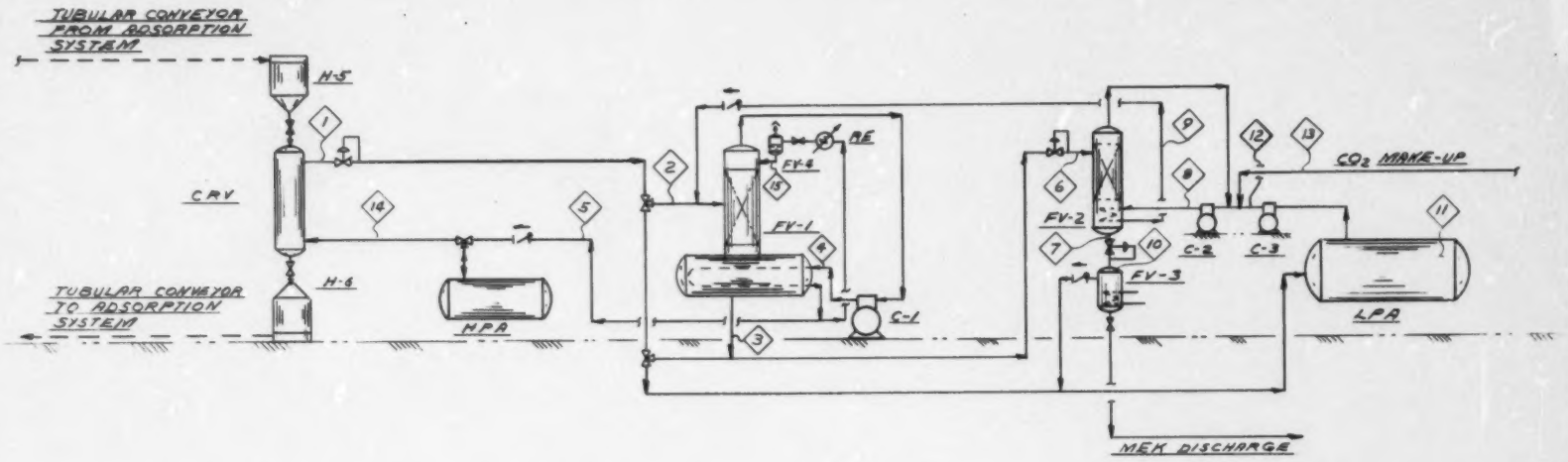
minutes, CRV is filled with the carbon in H5 and repressurized. The system is then in the state depicted in Figure IX.1C. The air flow is then switched to CA2, and the cycle begins again, as shown in Figure IX.1D.

Figure IX.2 is a flow schematic of the desorption and solvent recovery portion of the system. The CRV shown in Figure IX.2 is the same as that shown in Figure IX.1.

The desorption cycle operates as follows. Desorption at 100 atm and 50°C is carried out with continuous CO_2 flow for 10 minutes. At the completion of regeneration, the CRV is first depressurized into FV-1, the primary distillation unit, until the CRV pressure falls to 54 atm. At that point, the depressurization continues with CO_2 flow into FV-2, the secondary flash vessel, until the CRV pressure falls to 20 atm. Finally, the CRV is depressurized to 2 atm with CO_2 flow directed to the low-pressure accumulator, LPA. Following this, the remaining CO_2 is vented, and the carbon is discharged to the discharge hopper H-6.

The CRV is then charged with carbon from hopper H-5. During the CRW down-time, the high-pressure accumulator, HPA, is recharged from about 50 atm to 100 atm by continuing operation of the compressor C-1. After the carbon charge is received by CRV, the valve between the HPA and the CRV is opened, the pressure equalizes at about 50 atm, and the valve is closed. At that point, the CO_2 flow from compressor C-1 is redirected to the CRV to pressurize it to 100 atm as the desorption cycle is initiated.

During the desorption cycle, the desorber effluent, stream no. 1, leaves the CRV at 100 atm and 59°C. It is flashed through a valve to 54 atm and 20°C (stream no. 2) to the still FV-1. FV-1 is a small packed column with the equivalent of five theoretical plates in the rectifying section, and one theoretical plate in the stripping section. The overhead from FV-1 is fed to the suction side of the compressor C-1 to increase the pressure to 100 atm, with a concomitant temperature rise to 65°C.



PROCESS CONDITIONS	STREAM NO														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
PRESSURE PSIA	1500	800	800	1500	1500	300	300	800	800	14.7 TO 30	14.7 TO 30	300	300	1500	800
TEMPERATURE °C	50	20	50	66	57	21	47	82	60	16	16	82	-18	50	18
TEMPERATURE °F	122	68	122	150	135	70	117	180	140	60	60	180	0	122	65

LEGEND

- C-1 – COMPRESSOR
- C-2 – COMPRESSOR
- C-3 – COMPRESSOR
- CRV – CARBON REGENERATION VESSEL
- FV-1 – FLASH VESSEL
- FV-2 – FLASH VESSEL
- FV-3 – FLASH VESSEL
- H-5 – CARBON FEED HOPPER
- H-6 – CARBON DISCHARGE HOPPER
- HPA – HIGH PRESSURE ACCUMULATOR
- LPA – LOW PRESSURE ACCUMULATOR
- Fv-4 – FLASH VESSEL
- RE – REFLUX EXCHANGER

FIGURE IX.2

SUPERCRITICAL CO_2 V.O.C. CARBON REGENERATION SYSTEM

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The C-1 discharge is then fed to the FV-1 reboiler to provide the heat of vaporization, in a standard vapor recompression cycle. Approximately six mole percent of this stream is fed back to the still as reflux by undergoing cooling to 27°C, and being glashed to 54 atm where its quality becomes about 95% liquid, 5% vapor. At this point, a bleed of non-condensable gases may be taken, if necessary (FV-4), and stream no. 15, the column reflux, is reintroduced into FV-1. The remainder of the recompressed CO_2 (stream no. 5) returns to the column, undergoing slight cooling from 57°C to 50°C, where it is reintroduced to the CRV as clean make-up solvent.

The still bottoms from FV-1 leaves at 54 atm and 50°C, containing about 49 mole percent CO_2. It is directed to the flash vessel FV-2, maintained at 20 atm, and 21°C. The overhead from FV-2 is fed to compressor C-2, along with the required CO_2 make-up (available at 20 atm) and the discharge from compressor C-3, which empties the low pressure accumulator (LPA) from a pressure of 2 atm down to atmospheric pressure. The C-2 discharge (stream no. 8), at 54 atm and 82°C, provides the heat of vaporization for the flash in FV-2. The cooled 54-atm effluent (stream no. 9) is then added to the FV-1 feed to assure maximum removal of MEK from the CO_2.

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The bottoms liquid from flash vessel FV-2 is discharged into a small flash vessel FV-3, which operates at the pressure of the LPA, cycling between 2 atm and atmospheric pressure. Heat is added to provide essentially complete stripping of CO_2 from the final MEK discharge, using an electric heater. Thus, the MEK discharge is essentially free of CO_2. The FV-3 overhead is directed to the LPA.

B. SYSTEM DESIGN

The system is designed to handle 10,000 cfm containing one-quarter of the lower explosive limit (LEL) of methyl ethyl ketone, giving a feed concentration of 4,500 ppm. The capacity of GAC for MEK at 1.1×10^5 ppm feed was measured experimentally as 0.34 lbs/lb.

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For design purposes, it was assumed that the carbon would adsorb 75% of this level (0.26 lbs/lb carbon), since the MEK adsorption isotherm is relatively concentration independent at these concentration levels.

A 15-minute adsorption/desorption cycle was chosen by running optimization calculations with regard to vessel costs.

The above parameters fix the carbon bed size at 480 lbs of GAC, or about 18 ft^3. A figure of 20 ft^3 was used to fix the bed dimensions of both the adsorption and desorption vessel. In the adsorber, it was assumed that the bed depth would be about 4", utilizing a square vessel with a dimension of about 7' on the side. The desorber was dimensioned to give reasonable pressure-vessel parameters, and was taken as a 2' diameter, 7' length vessel.

Sizing of the flash vessels was based on established capacity correlations for packed or open vessels. The sizing of the high-pressure and low-pressure accumulators was based on the gas volumes involved. Details of these calculations are presented in Appendix B.

Figure IX.3 shows the material balance on CO_2 flow around the CO_2 recovery system.

C. PROCESS ECONOMICS

Table IX.1 summarizes the system capital cost. As shown, vendor's estimates or estimates based on standard correlations were used to obtain the costs of the individual equipment items. Following the cost-estimating practice described by Guthrie (1969), installation factors were used to give so-called module costs for each item, and these were summed to give the installed costs for the system. As recommended by Guthrie, a 10% contingency plus a 3% contractor's fee was added, to give a system cost of $530,000. These cost figures represent December, 1980 costs.

FIGURE IX.3

CO_2 FLOW RATES FOR MEK/CO_2 SEPARATION SYSTEM

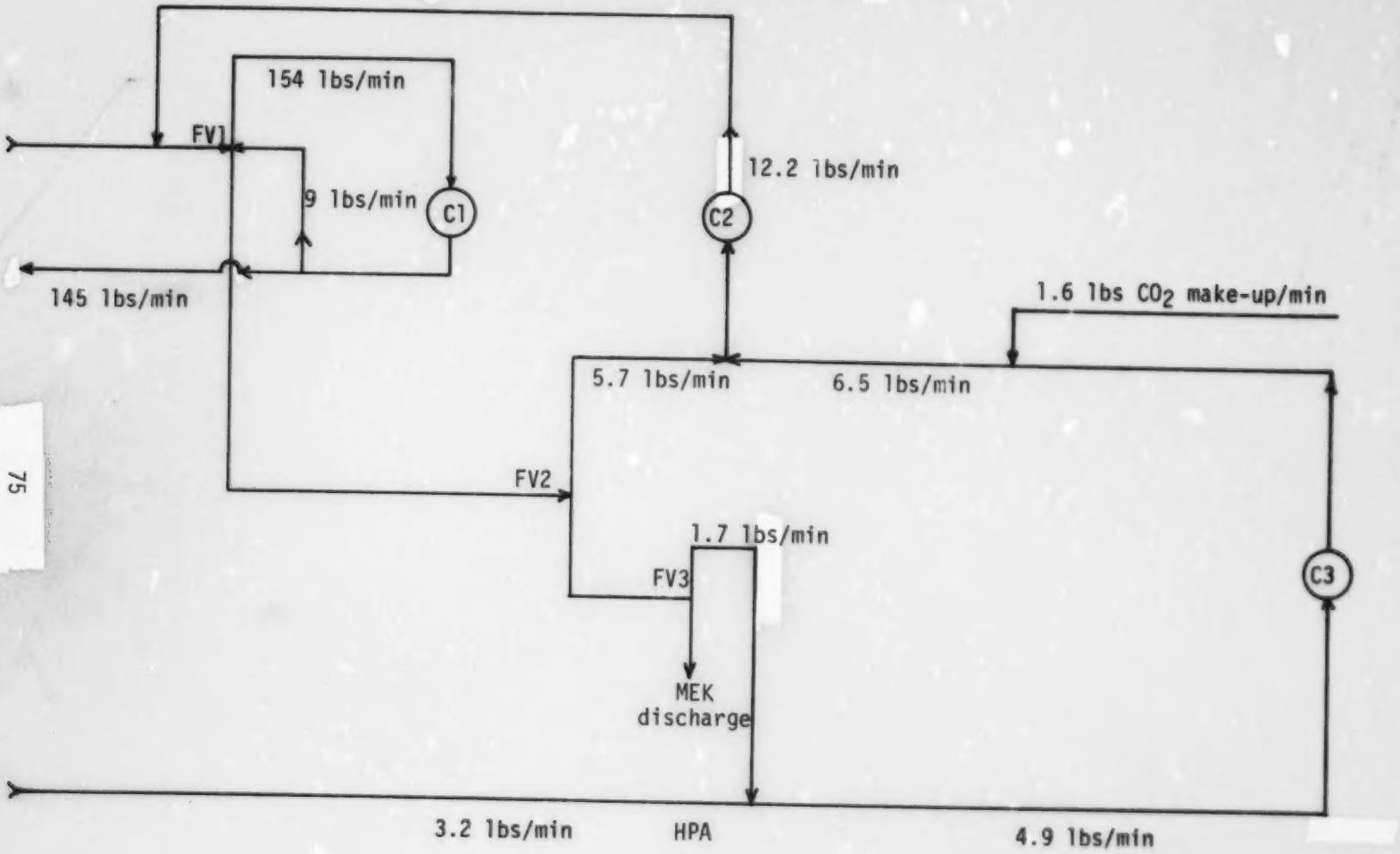

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TABLE IX.1

CAPITAL COST ESTIMATE

Capacity: 10,000 SCFM Air laden with 1/4 LEL of MEK
$ Basis: December, 1980
(000 omitted)

DESORPTION SYSTEM

Equipment Item	Skid Cost, $		Installed Cost,$
Compressor C1	48.0		
Compressor C2	31.2		
Compressor C3	25.4		
	104.6		
	+ 20.9	(20% Installation Factor[1])	
	125.5		
	+ 25.1	(20% Engineering, Indirects)	
	150.6		150.6

	Total Equipment Cost,$	Modular Factor[2]	
Carbon Regeneration CRV	24.49	4.23	103.6
Separator FV1	4.54	4.23	19.2
FV1 Heat Exchanger	9.56	3.28	31.4
Separator FV2	1.46	4.23	6.2
FV2 Heat Exchanger	1.30	1.83	2.4
Separator FV3	0.80	4.23	3.4
Separator FV4	2.06	4.23	8.7
Reflux Heat Exchanger	3.11	1.83	5.7
Accumulator HPA	11.88	3.18	37.8
Accumulator LPA	3.90	3.18	12.4
			381.4

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ADSORPTION SYSTEM

Equipment Item	Total Equipment Cost,$	Installation,$	
Carbon Adsorber X2			15.5
Carbon Hoppers X6	15.0	4.0	19.0
Tubular Conveyor	18.0	2.0	20.0
Misc. Feeders, Control	5.0	3.5	8.5
Fan			3.7
Carbon			4.8
			71.5

DESORPTION SYSTEM	$381.4		
ADSORPTION SYSTEM	89.4	(25% Engineering, Indirects) +	17.9
	470.8		89.4
+ 10% Contingency + 3% Fee	61.2		
	$532.0		

1. Skid-mounted reciprocating compressor installation factor.
2. Guthrie, 1969.

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Operating costs for the system are presented in detail in Table IX.2. T, IX, 2 These sum to a cost of about 2¢/lb of GAC regenerated. Both capital costs may be compared with those published for other carbon regeneration systems that were summarized in Table IV.3. The highest-cost system shown among competitive processes is about $450,000. That system, which involves steam regeneration, produces a mixture of MEK and water, which has a low value as solvent to be recycled to the industrial operation. The MEK discharge from the CO_2 system is essentially free of water, and thus could be valued at close to make-up MEK prices.

On this basis, it is possible to carry out an approximate pay-out calculation for the system, assuming full value for recovery of MEK. The calculation shows that the annual MEK value, reduced by the annual operating costs of the entire carbon regeneration system, comes to $1,100,900/year. Dividing this into the capital cost of $530,000 gives a rough pay-out time of approximately 0.48 years. Thus, if good-purity MEK can be recovered from the system, the carbon regeneration process provides an opportunity for a rapid pay-out source of make-up industrial solvent.

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TABLE XI.2

PROCESS COST ESTIMATE

Case: Supercritical Carbon Dioxide Regeneration of Activated Carbon Used for MEK Vapor Adsorption

Capacity: 10,000 SCFM Air laden with 1/4 LEL of MEK = 12,000 lb MEK/day; 46,100 lb GAC regenerated/day

Capital Investment: $532,000 (Basis: December, 1980)
Operation: 330 days/yr

Variable Costs

	Unit/Day	$/Unit	$/day	¢/lb MEK Recovered
Electricity :	2208 KWH	0.05	110.40	0.920
Make-up CO_2 :	2304 lbs	0.08	184.32	1.536
Cooling H_2O :	2.448 Mgal	0.15	0.37	0.003
Make-up Carbon:	10% Carbon Inventory†/yr		1.45	0.012
	Total Variable Costs:		296.54	2.471

Semi-variable Costs

Operating Labor:	1/2 man/shift, 3 shift/day @ $11.00/hr	132.00	1.100
Supervision :	1/4 man/yr @ $30,000/yr	22.73	0.189
Labor Overhead :	60% of Labor & Supervision	92.84	0.774
Maintenance :	4% of Capital Investment/yr	64.48	0.537
	Total Semivariables:	312.05	2.600

Fixed Costs

Plant Overhead :	40% of Labor & Supervision	61.89	0.516
Depreciation :	10% of Capital Investment/yr	161.21	1.343
Taxes & Insurance :	2% of Capital Investment/yr	32.24	0.269
	Total Fixed Costs:	255.34	2.128

Total Operating Cost: $863.93/day
7.199 ¢/lb MEK recovered
1.87 ¢/lb GAC regenerated

† for fixed-bed adsorber system.

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XI. APPENDICES

APPENDIX A. EQUILIBRIUM AND MASS-TRANSFER PROPERTIES OF SUPERCRITICAL FLUIDS (Adapted from de Filippi, et al., 1980)

The supercritical fluid region can best be visualized with the aid of a reduced pressure-density diagram, shown in Figure XI.A.1. The dashed curve is the locus of liquid-vapor equilibria, which terminates at the critical point CP. The reduced density ρ_r (= ρ/ρ_{CP}) of the normal liquid is about 2.6; the critical density is about 40% of that of the normal liquid.

The SCF region, as the term is used here, refers to the region defined by reduced temperature T_r (=T/T_{CP}) between 1 and 1.4 and reduced pressures P_r (=P/P_{CP}) from 1 to 6. The near-critical liquid (NCL) region is the region bounded by $0.95 \leq T_r \leq 1.0$ and P_r from that of saturated liquid to 6. In the SCF and NCL regions, fluid densities are high enough to exhibit liquid-like solubility behavior, yet low enough that diffusivities are appreciably higher than those of normal liquids.

Although there is sufficient evidence to show that solid and liquid solutes have unusually high solubilities in supercritical fluids (see, e.g., Paul and Wise, 1971), few systems have been extensively investigated. One system that has been studied in some depth is naphthalene (m.p. 58°C) in CO_2 (T_{CP} = 31.0°C, P_{CP} = 72.9 atm). The data of Tsekhanskaya, et al., (1964) and Quinn and Jones (1936), have been interpolated and extrapolated into a 'map' of solubility over a wide range of conditions, as shown in Figure XI.A.2. The dashed curve represents the solubility in saturated liquid and vapor. At the critical point, the solubility is 0.23 mole-% naphthalene; at 300 atm and 50°C, it is about 4 mole-%, which is equivalent to 11 wt.%. At high pressures (150-300 atm), the solubility increases with increasing temperature. This solubility behavior is the result of increasing activity (or vapor pressure) of the solute with increasing temperature. On the other hand, at pressures near the critical (70-80 atm), there is an inverse solubility relationship; solubility <u>decreases</u> dramatically

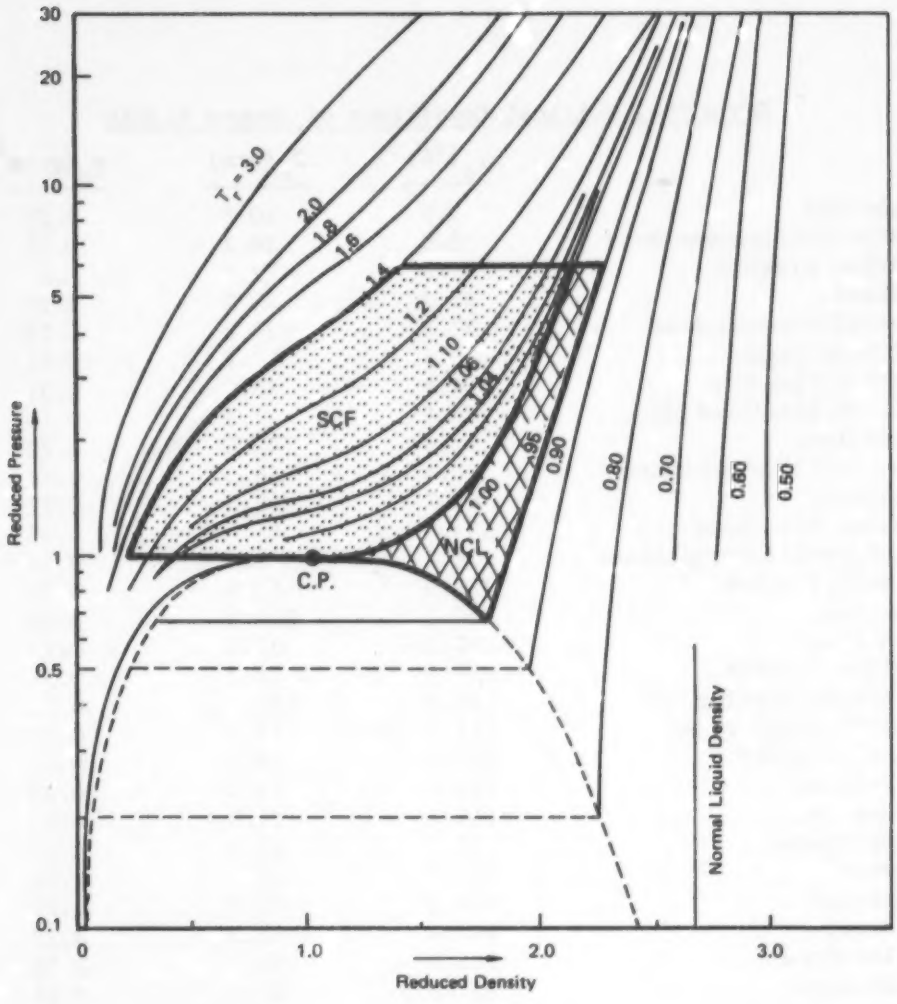

FIGURE XI.A.1 - **REDUCED PRESSURE-DENSITY DIAGRAM. SUPERCRITICAL FLUID (SCF) AND NEAR-CRITICAL LIQUID (NCL) REGIONS, AS INDICATED**
(Copyright 1968 by the American Association for the Advancement of Science; reproduced courtesy of Giddings, Science, 162:67-73)

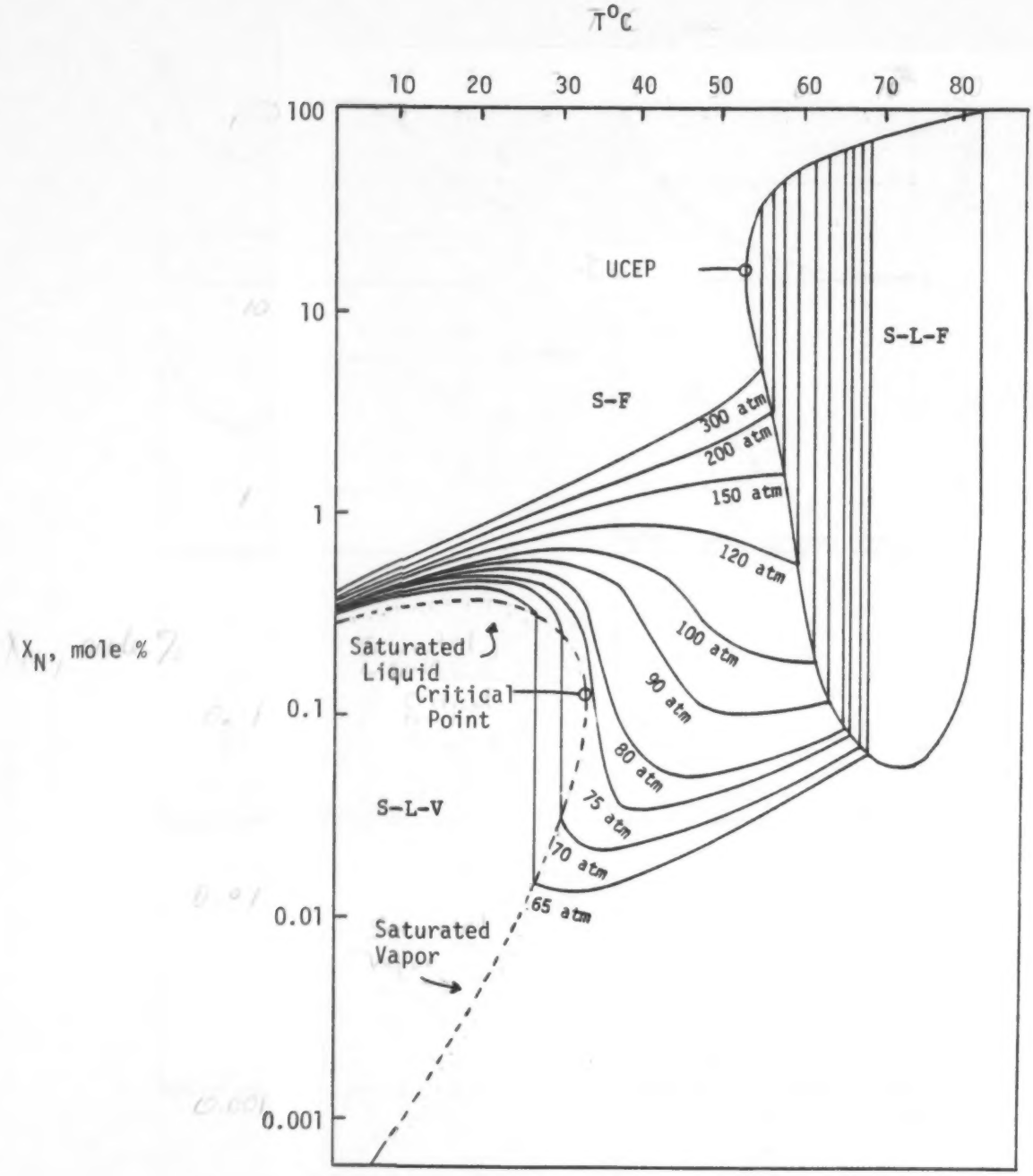

FIGURE XI.A.2 - SOLUBILITY MAP OF NAPHTHLANENE IN NCL and SCF CARBON DIOXIDE

(From Modell, et al., 1979)

with increasing temperature because the density of the solvent is decreasing rapidly with small change in temperature (see Figure XI.A.1). At temperatures above the upper-critical-end-point temperature, approximately 52°C for the CO_2-naphthalene system, a three-phase region of solid/liquid/fluid exists.

There is reason to expect that the solubility behavior shown in Figure XI.A.2 is representative of a broad range of solid solutes in supercritical fluids. For instance, the silica/water system has the solubility map shown in Figure XI.A.3. The similarities in the shapes of the isobars for the CO_2-naphthalene and SiO_2-H_2O systems are striking. The solubility behavior shown in Figures XI.A.2 and 3 results from the interplay of secondary valence forces between molecules in solution. These forces are the same ones that result in departure from ideal gas behavior. If accurate equations of state for the mixture are available, then it is possible to predict the solubility behavior from the criterion of equilibrium, i.e., equality of chemical potential or fugacity in each phase for each component.

Modell, et al. (1979), showed that the Peng-Robinson (PR) equation of state (Peng and Robinson, 1976), a modification of the Redlich-Kwong equation of state, can predict phase equilibria for the CO_2-naphthalene system in the sub- and supercritical regions with reasonably accuracy. The PR-predicted solubilities of naphthalene in CO_2 are in reasonable accord with the data presented in Figure XI.A.2; the PR equation also predicted the presence of the three-phase solid/liquid-fluid region and its upper-critical-end-point temperature of 52°C.

Francis and Paulitis (in press) have used the Lee-Kesler equation of state to quantitatively predict phase equilibria for the ethylene-naphthalene and ethane-naphthalene systems in the SCF region. They found a temperature-pressure solubility dependence similar to that for the CO_2-naphthalene system, and also the three-phase region at higher temperatures. Thus, it is believed that the solubility maps shown in Figures XI.A.2 and 3 are representative of the behavior of a range of solid solutes in supercritical fluids.

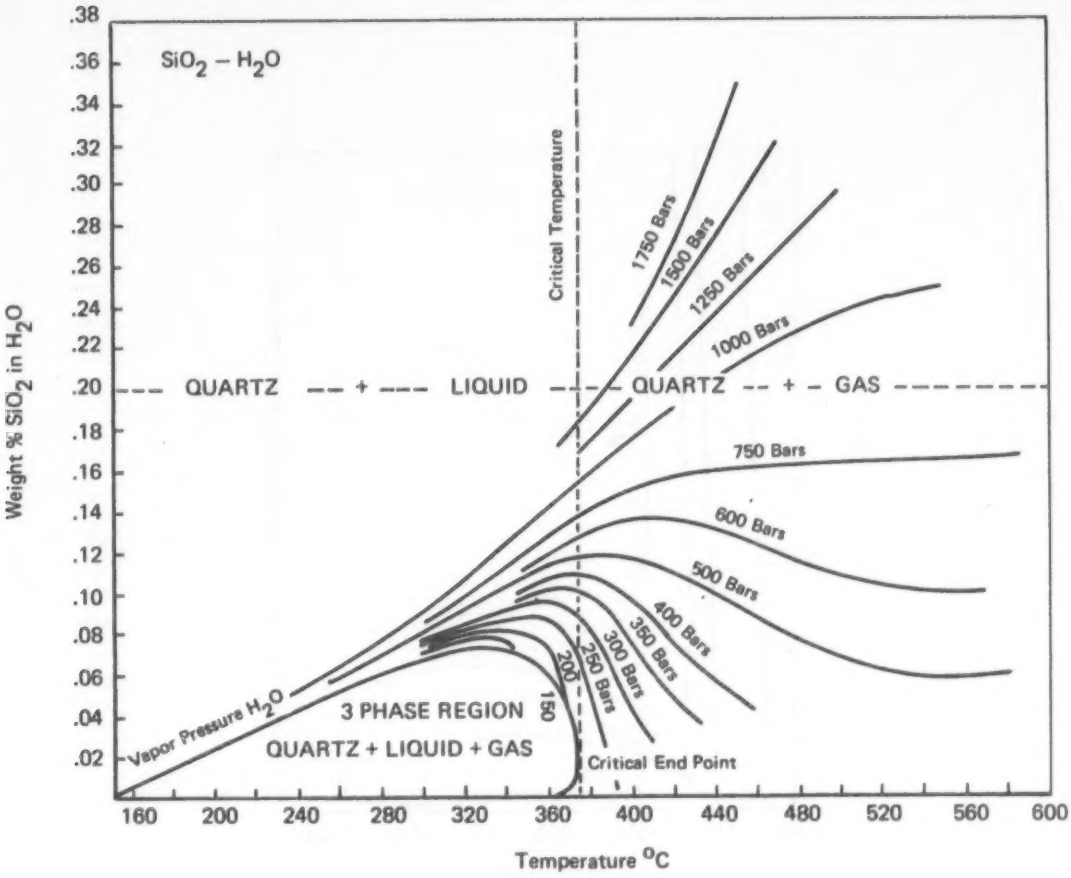

FIGURE XI.A.3 - SOLUBILITY OF SiO_2 IN H_2O (KENNEDY, 1950)

While there is a paucity of data in the literature concerning the solubilities of organic solids and liquids in supercritical fluids, there is a large body of data on solubilities in near-critical liquids. For example, Francis (1954) reported the mutual solubilities of NCL CO_2 at 25°C with each of 261 organic substances (Table XI.A.1). Each of these solubilities represents a single data point on a solubility map. For example, Francis reports the solubility of naphthalene in liquid CO_2 at 25°C as 2 wt.%. In Figure XI.A.2, the corresponding point lies on the saturated liquid curve at 25°C, which is 0.62 mole-% or about 2 wt.%. Thus, Francis' data can be used as a guide for the magnitude of solubility in the critical region. It should be noted that nearly half of the compounds studied were completely miscible with NCL CO_2. The naphthalene solubility behavior discussed above is representative of the less soluble organics in CO_2.

From Figure XI.A.2, it is seen that solubility at high pressure (150-300 atm) and supercritical temperature can be substantially higher than the solubility in saturated liquid at 25°C. At some point of higher pressures and temperatures, solutes that are only slightly soluble at 25°C will become completely miscible. Such critical loci have been reported for a number of organics with CO_2 (Schneider, 1970). The pressure-temperature projections of the critical loci for mixtures of CO_2 and several alkanes is shown in Figure XI.A.4 (Liphard, 1975). For octane, there exists a continuous vapor-liquid critical locus connecting the critical points of the pure materials. There is also a liquid-liquid critical locus that exists at low temperatures. To the right of the L-L critical and above the L-G critical, only one phase exists; in that region, octane and CO_2 are completely miscible. Note from Table XI.A.1 that both heptane and dodecane are completely miscible with liquid CO_2 at 25°C; thus, octane would also be completely miscible at 25°C, which is in accord with the data in Figure XI.A.4. For tridecane and higher molecular weight alkanes, the L-G and L-L critical loci merge into a single, continuous critical locus. To the upper right side of the critical locus, the system is completely miscible; below it and to the left, the

TABLE XI.A.1 SOLUBILITIES OF ORGANIC COMPOUNDS IN LIQUID CO_2 AT 25°C and 65 ATM. (From Francis, 1954)
(Solubilities in weight-percent; M = completely miscible)

Paraffins and Naphthenes	
n-Butane	M
Cyclohexane	M
Decahydronaphthalene	22
2,2-Dimethylpentane	M
n-Dodecane	M
Ethane	M
n-Heptane	M
n-Hexadecane	8
Methylcyclohexane	M
n-Octadecane (mp 28 C)	3
Paraffin wax (mp 52 C)	1
Propane	M
n-Tetradecane	16
2,2,3-Trimethylbutane	M

Olefins	
1-Decene	M
1-Octadecene	10
Propylene	M

Aromatics	
Benzene	M
Bibenzyl (mp 52.5 C)	1
Biphenyl (mp 71 C)	2
Chlorobenzene	M
α-Chloronaphthalene	1
Di-sec-butylbenzene	M
p-Dichlorobenzene (mp 53 C)	M
α,α-Dichlorotoluene	M
p-Dimethoxybenzene (mp 53 C)	M
Dimethylnaphthalenes (mixed)	2
Diphenylmethane (mp 27 C)	4
o-Hydroxybiphenyl (mp 56 C)	1
2-Methoxybiphenyl (mp 29 C)	5
α-Methylnaphthalene	6
β-Methylnaphthalene (mp 35 C)	9
Naphthalene (mp 52 C)	2
Nitrobenzene	M
o-Nitrochlorobenzene (mp 32)	21
α-Nitronaphthalene (mp 58 C)	1
o-Nitrotoluene	M
p-Nitrotoluene	20
Tetrahydronaphthalene	12
Toluene	M

Alcohols	
t-Amyl alcohol	M
Benzyl alcohol	8
sec-Butyl alcohol	M
β-Chloroethanol	10
Cinnamyl alcohol (mp 30 C)	5
Cyclohexanol	4
1-Decyl alcohol	1
β-Ethoxyethanol	M
2-Ethylhexanol	17
Ethyl alcohol	M
Furfuryl alcohol	4
Heptyl alcohol	6
Hexyl alcohol	M
Isopropyl alcohol	M
Methyl alcohol	M

Aldehydes	
Acetaldehyde	M
Benzaldehyde	M
Cinnamaldehyde	4
Crotonaldehyde	M
1-Heptaldehyde	M
Paraldehyde	M
Propionaldehyde	M
Salicylaldehyde	M
Valeraldehyde	M

Ketones	
Acetone	M
Acetophenone	M
Benzalacetone (mp 42 C)	5
Benzophenone (mp 48 C)	4
2-Butanone	M
Chloroacetone	M
Cyclohexanone	M
2,5-Hexanedione	M
2-Octanone	M

Ethers	
S-Butyl ether	M
β,β'-Dichloroethyl ether	M
Ethyl ether	M
Isopropyl ether	M
Phenyl ether (mp 28 C)	8

Phenols	
o-Chlorophenol	M
p-Chlorophenol (mp 43 C)	8
p-Chloro-6-phenylphenol	1
o-Cresol (mp 30 C)	2
m-Cresol	4
p-Cresol (mp 36 C)	2
2,4-Dichlorophenol (mp 45 C)	14
p-Ethylphenol (mp 46 C)	1
o-Nitrophenol (mp 45 C)	M
Phenol (mp 41 C)	3

Esters	
Benzyl benzoate	10
Butyl oxalate	M
Butyl phthalate	8
Butyl stearate	3
β-Chloroethyl acetate	M
Ethyl acetate	M
Ethyl acetoacetate	M
Ethyl benzoate	M
Ethyl chloroacetate	M
Ethyl chloroformate	M
Ethylene diformate	M
Ethyl formate	M
Ethyl lactate	M
Ethyl maleate	M
Ethyl oxalate	M
Ethyl phenylacetate	M
Ethyl phthalate	10
Ethyl salicylate	M
Ethyl succinate	M
β-Hydroxyethyl acetate	17
Methyl benzoate	M
Methyl phthalate	6
Methyl salicylate	M
Phenyl phthalate (mp 70 C)	1
Phenyl salicylate (mp 43 C)	9

Amides	
Acetamide (mp 82 C)	1
N,N-Diethylacetamide	M
N,N-Diethylformamide	M
N,N-Dimethylformamide	M
Formamide	0.5

Carboxylic Acids	
Acetic acid	M
Caproic acid	M
Caprylic acid	M
Chloroacetic acid (mp 61 C)	10
α-Chloropropionic acid	26
Formic acid	M
Isocaproic acid	M
Lactic acid	0.5
Lauric acid	1
Oleic acid	2
Phenylacetic acid (mp 77 C)	0

Amines and Nitrogen Heterocyclics	
Aniline	3
o-Chloroaniline	5
m-Chloroaniline	1
N,N-Diethylaniline	17
N,N-Dimethylaniline	M
Diphenylamine (mp 53 C)	1
N-Ethylaniline	13
N-Ethyl-N-benzylaniline	4
N-Methylaniline	20
α-Naphthylamine (mp 52 C)	1
Phenylethanolamine	1
2,5-Dimethylpyrrole	5
Pyridine	M
o-Toluidine	7
m-Toluidine	15
p-Toluidine (mp 45 C)	7

Nitriles	
Acetonitrile	M
Acrylonitrile	M
Benzonitrile	M
β-Hydroxypropionitrile	1
Phenylacetonitrile	13
Succinonitrile (mp 54.5 C)	2
Tolunitrile (mixed)	M

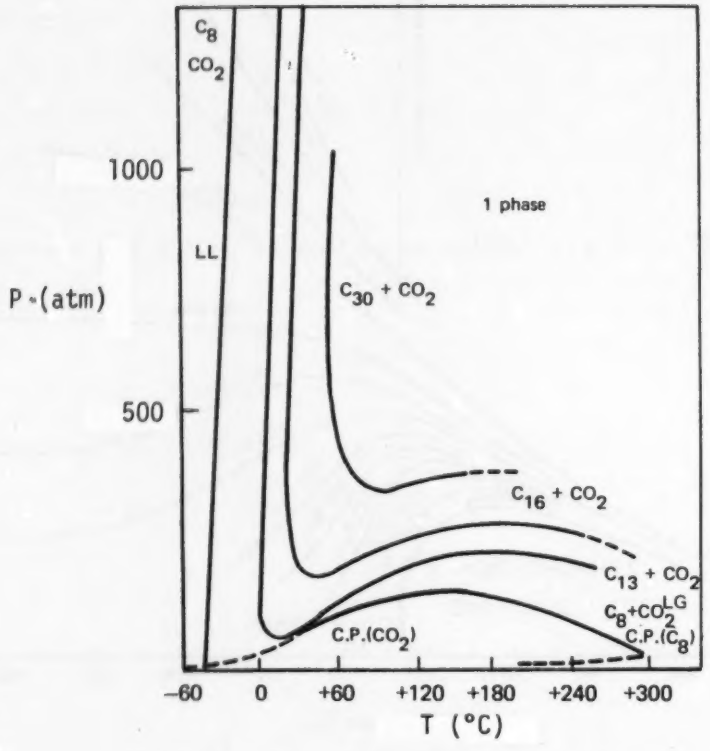

FIGURE XI.A.4

P–T PROJECTIONS OF THE PHASE DIAGRAMS AND CRITICAL LOCI OF BINARY CO_2 + ALKANE MIXTURES. FULL LINES, CRITICAL CURVES; BATCHED LINES, VAPOR PRESSURE CURVES OF CARBON DIOXIDE AND OCTANE, RESPECTIVELY.

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NOTE: C_8, C_{13} and C_{18} are normal alkanes; C_{30}= squalane

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system exhibits two or more phases of limited miscibility. Note that for hexadecane at 25°C, the critical point occurs at around 250 atm. At 25°C and pressures below 250 atm, the hexadecane-CO_2 system exists as two phases. At 25°C and 65 atm, Table XI.A.1 lists a solubility of 8 wt.% hexadecane in the CO_2-rich phase. Reasoning in the converse manner, it might be anticipated that those substances exhibiting limited solubility in liquid CO_2 at 25°C would be completely miscible with CO_2 at higher pressures and temperatures.

This brief discussion of solubility phenomena in the critical region illustrates several important generalities:

(1) Enhanced solubility in the critical region is a general phenomenon that arises from the interplay of secondary valence forces.

(2) Partially miscible systems at NCL conditions tend to complete miscibility at supercritical conditions.

(3) A large number and variety of organic compounds are partially or completely miscible with CO_2 in the near- and supercritical-fluid regions.

Mass Transfer Properties

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Several investigators have measured self-diffusivity of CO_2 in the sub- and supercritical region (for a compilation, see Vargaftik, 1975). These data have been correlated and developed into a map of self-diffusivity, as given in Figure XI.A.5. In liquid CO_2 at 25°C, the diffusivity is about an order of magnitude higher than that of conventional liquid solvents. The vapor diffusivity at 25°C is another factor of 10 higher. At supercritical temperatures, the diffusivities vary between 10^{-3} and 10^{-4} cm^2/sec; decreasing from the higher to lower values with increasing density.

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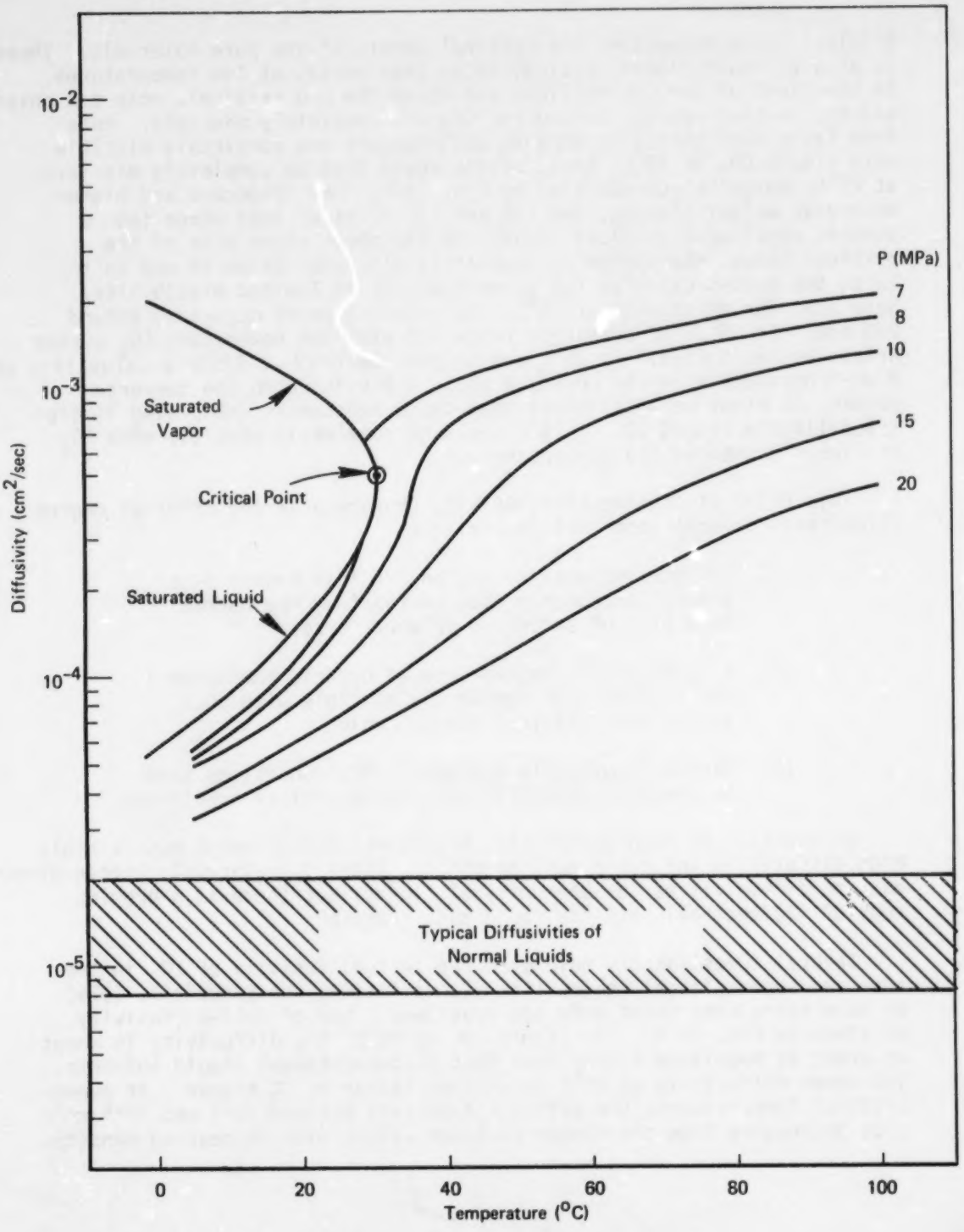

FIGURE XI.A.5-DIFFUSIVITY OF CARBON DIOXIDE IN THE SCF AND NCL REGIONS

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By comparison of Figures XI.A.2 and XI.A.5, it can be seen that the decrease in diffusivity with density is less than the increase in solubility with density: at 40°C, the diffusivity decreases from 80 atm ($8x10^{-4}$ cm^2/sec) to 120 atm ($1.5x10^{-4}$) by a factor of 5.3, while the solubility increases from 80 atm (0.1 mole-%) to 120 atm (1.2 mole-%) by a factor of 12. Thus, it is seen that the gain in solubility at higher density more than outweighs the decrease in diffusivity. Furthermore, the diffusivities in the SCF range are at least an order of magnitude higher than those of conventional liquid solvents.

As a result of the unique characteristics of high solubility and rapid mass transfer, there is increasing interest in exploiting supercritical fluids as extracting agents. A number of recent French and German patents describe the use of SCF CO_2 to extract caffeine from coffee and tea (Hag, 1973, a,b), cocoa butter from pulverized kernels (c), aroma constituents from pepper, cloves, cinnamon and vanilla beans (d), and selective extraction of nicotine from tobacco (e). The extracts are free of trace impurities that would stem from the use of organic liquid solvents. Furthermore, degradation of heat-sensitive solutes is avoided because the processes employ mild temperatures, in the range of 30 to 60°C. Supercritical fluids have also been investigated as potential extracting agents for crude petroleum and residual oil (Zhuze, 1957), coal tar (Wise, 1970) and coal (Maddocks, 1979).

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APPENDIX B. DESIGN CALCULATIONS

1. Carbon Needed

10,000 CFM air mixture ÷ 389 ft^3/lb mol (@ 73°F)

= 25.7 lb mols air mixture/minute.

MEK LEL = 1.8% take ¼ LEL = 0.45% = 4500 ppmv

$$25.7 \text{ mols mixture/min} \times \frac{0.0045 \text{ mol MEK}}{\text{mol mix}} = 0.1157 \text{ mols } \frac{\text{MEK}}{\text{min}}$$

$$0.1157 \frac{\text{mols MEK}}{\text{min}} \times 72 \text{ lb } \frac{\text{MEK}}{\text{mol}} = 8.33 \text{ lb MEK/min}$$

(= 500 lb MEK/hr)

(= 12,000 lb MEK/day)

Experimental carbon loading with MEK feed ≈ 1.3 x 10^5 ppmv

= 0.34 lb MEK/lb carbon. Loading with MEK feed = 4500 ppmv extrapolated to be 0.26 lb MEK/lb carbon (isotherms relatively flat).

8.33 lb MEK/min ÷ 0.26 lb MEK/lb carbon = 32 lb carbon/min

Experimental packing of Calgon BPL 12 x 30 Mesh GAC = 0.42 g/cc

$$0.42 \text{ g/cc} \times \frac{1000 \text{ cc/ℓ}}{454 \text{ g/lb}} \times \frac{28.316 \text{ ℓ}}{ft^3} = 26.2 \text{ lb/ft}^3$$

For long desorption cycle length, i.e., 30 minutes or more, desorption vessel becomes large and very expensive. Very short desorption cycle length, i.e., several minutes, increased valve cycling and wear and increased carbon handling. Rough optimization calculations show 15 minute desorption cycle to be desirable; therefore, there is a 15 minute adsorption cycle.

32 lb carbon/min x 15 min = 480 lb carbon/15 min cycle

$$\frac{480 \text{ lb carbon}}{15 \text{ min cycle}} \div \frac{26.2 \text{ lb carbon}}{ft^3} = 18.3 \text{ ft}^3 \text{ carbon/15 min cycle; say, } 18.5 \text{ ft}^3.$$

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2. Adsorption System

10,000 cfm air stream. Adsorption bed superficial velocity limited by bed pressure drop. Superficial velocity typically specified in the range of 50-100 ft/min where pressure drop for typical GAC is less than 10" H_2O/ft of bed depth (manufacturers supply a log (pressure drop) vs log (superficial velocity) for their carbon). Anticipate shallow bed, so high superficial velocity permissible; might run into mass-transfer limitations, however. Select superficial velocity = 200 ft/min = 2.3 mile/hr.

10,000 cfm ÷ 200 ft/min = 50 ft^2 of bed surface normal to air stream.

Carbon bed depth = $\frac{18.5\ ft^3}{50\ ft^2}$ carbon x $\frac{12"}{ft}$ = 4.4" deep.

Pressure drop dense-packed 12 x 30 mesh PCB carbon = 30" $\frac{H_2O}{ft\ bed}$ @ superficial velocity = 200 ft/min

$\frac{30"\ H_2O}{12"\ bed}$ x 4.4" = 11.0" H_2O pressure drop; loosely packed beds (26 lb/ft^3) give pressure drop approximately one-third of the dense bed, according to the manufacturer, so 11" ÷ 3

≅ 4" H_2O pressure drop for carbon bed. Add in pressure drop for ancillary ductwork, screens, etc., say total is 2x carbon pressure drop = 8" H_2O.

Hopper system operation described in Section IX.A. Carbon is fed into adsorber from top; adsorber is two parallel screens 4.4" apart, $\sqrt{50'}$ = 85" on a side, inside a sheet metal housing with necessary baffles to provide air flow normal to the adsorber beds.

Fan to provide 10,000 cfm air at 8" H_2O pressure drop, backward curved fan, Class II, $1200 (11/78); 20 HP explosion-proof motor, 1800 RPM $300 x 1.6 = $480 (11/78); $1680 x $\left(\frac{273}{219}\right)$ (price index ratio) = $2100 (12/80)

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(Neveril, et al., 1978) + labor + indirects = $3700.

Carbon Adsorber assembly -- screens + housing + baffles

2 x $7.75k, installed (from vendor)

Tubular Conveyor System, 100 ft x 4' diameter, Hapman Conveyor Co.,

$18k + $2k assembly.

Carbon Hoppers, 6 x $2500 + $4k installation

Misc. feeders, junctions, ductwork $5k + $3.5k labor

Carbon: 5 x 480 lbs x $2.00/lb for (attrition resistant carbon) = $4.8k

Cost Summary & Basis: December, 1980 (000 omitted)

Equipment Item	Total Equipment Cost, $	Installation, $	
Carbon Adsorber X2			$ 15.5
Carbon Hoppers X6	15.0	4.0	19.0
Tubular Conveyor	18.0	2.0	20.0
Misc. Feeders, Control	5.0	3.5	8.5
Fan			3.7
Carbon			4.8
			71.5
		(25% Engineering, Indirects)	+ 17.9
			$ 89.4

3. CO_2 Circulation Rate

$$8.33 \frac{\text{lb MEK}}{\text{min}} \left[\frac{14 \text{ SL } CO_2}{2.29 \text{ g MEK}}^{*} \times \frac{1.82 \text{ g } CO_2}{\text{SL } CO_2} \times \frac{454 \text{ g MEK/lb MEK}}{454 \text{ g } CO_2/\text{lb } CO_2} \right]$$

= 93 lb CO_2/min, continuous rate

*Table VII.5, Cycle 2

desorbing for 10 min of the 15 min cycle, so (15/10) times the CO_2 circulation rate is needed.

93 lb CO_2/min x 1.5 = 140 lb CO_2/min = flow rate CO_2 during 10 minute desorption.

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4. Desorption vessel -- "Carbon Regeneration Vessel (CRV)"

For operation at 1500 psia and 50°C

Material = 316 SS clad carbon steel

S = allowable stress = 18,750 psi

E = joint efficiency = 1.0 (100% X-rayed)

P = design pressure, say, 1600 psi

R = inner radius = 11"

t = wall thickness, inches

$$t = \frac{PR}{SE-0.6P} = \frac{(1600)(11)}{18{,}750 - (0.6)(1600)} = 0.99"$$

therefore, have OD = 24", ID = 22"

Internal cross-sectional area = 2.64 ft^2

For 20 ft^3 volume, L = 20/2.64 = 7.6 ft

Cost, vertical fabrication (Guthrie, 1969)

= base cost x Fm x Fp x CAF x price index

$$= \$1000 \times 2.25 \times 4.35 \times 1.1 \times \left(\frac{273}{120}\right) = \$24.49k \quad (Dec., 1980)$$

Installed cost = cost x modular factor = \$24.49k x 4.23

= \$103.6k

5. CO_2/MEK Separation

800 PSIA

Feed: CO_2 = 0.952, MEK = 0.048

Desired overhead purity: CO_2 = 0.999995, MEK = 0.000005
Bottoms composition at 50°C CO_2 = 0.49, MEK = 0.51

CO_2: $0.952 = 0.999995V + 0.49L$
MEK: $0.048 = 0.000005V + 0.51L$

$$L = \frac{\left(\frac{0.999995}{.000005}\right) 0.048 - 0.952}{\left(\frac{0.999995}{.000005}\right) 0.51 - 0.49}$$

$= 0.094$; $V = 0.906$

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That is, with bottoms at 50°C and overhead purity specified above, 90.6% of feed goes overhead as vapor.

Feed rate is: 3.633 lb mole mixture/min
3.459 lb mole CO_2/min
152.2 lb CO_2/min

Overhead: 3.292 lb mole CO_2/min
144.9 lb CO_2/min

Bottoms: 0.167 lb mole CO_2/min
7.3 lb CO_2/min

Use Smoker equation (Smith, 1963, pp. 155-160) to determine number of stripping and rectifying stages.

$y_D = 0.999995$

$$x_D = \frac{1}{\alpha\left(\frac{1}{y_D} - \frac{(\alpha-1)}{K}\right)}$$

α from Table VIII.1 = 33.9

$x_D = 0.99983$

Rectifying section calculation for 6% reflux case.

$$m = \frac{R}{R+1} = \frac{0.06}{1.06} = 0.0566$$

$$b = \frac{x_D}{R+1} = \frac{0.99983}{1.06} = 0.943$$

operating line: $y = 0.0566x + 0.943$

$$m(\alpha-1)x^2 + \left[m + b(\alpha-1) - \alpha\right]x + b = 0$$

$x_1 = 0.4991 = K$

q-line: $y = \frac{q}{q-1}x - \frac{x_F}{q-1} = -0.4286x + 1.3571$

intersection of operating and q-lines: $x_n = 0.853$

$X_o' = X_D - K = 0.5007$

$X_n' = X_n - K = 0.354$

$C = 1 + (\alpha - 1)K = 17.42$

$$\frac{mc(\alpha - 1)}{(\alpha - mc^2)} = 1.94$$

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$\frac{K}{mc^2} = 1.974$

Using Smoker equation with the above-calculated values, n = 4.03

Stripping-section stage calculation for 6% reflux case.

Operating line slope and intercept --

$$m = \frac{R\,X_F + qX_D - (R + q)\,X_B}{(R+1)X_F + (q-1)X_D - (R+q)\,X_B} = 1.381$$

$$b = \frac{(X_F - X_D)\,X_B}{(R+1)X_F + (q-1)X_D - (R+q)X_B} = -0.1868$$

intersection of operating line with q-line:

$$X_o = 0.853$$

$$m(\alpha - 1)x^2 + \left[m + b(\alpha-1) - \alpha\right]x + b = 0$$

$X_1 = 0.869 = K$

$X_o' = 0.853 - 0.869 = -0.016$

$X_n' = 0.49 - 0.869 = -0.38$

$c = 1 + (32.9)(0.869) = 29.59$

$mc^2 = 1209.2$

$\frac{mc(\alpha - 1)}{\alpha - mc^2} = -1.1439$

Using Smoker equation with the above calculated values,

n = 1.04

Total Stages = 4.03 + 1.04 = 5.07; Round up-- 6 theoretical stages.

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300 PSIA

Feed: CO_2 = 0.49, MEK = 0.51

Overhead purity at flash temp: CO_2 = 0.991, MEK = 0.009
Bottoms composition at 47°C: CO_2 = 0.18, MEK = 0.82

CO_2: 0.49 = 0.991V + 0.18L
MEK: 0.51 = 0.009V + 0.82L

L = 0.62, V = 0.38

Feed rate is: 0.3415 lb mole mixture/min

Overhead: 0.129 lb mole CO_2/min
5.7 lb CO_2/min

Bottoms: 0.038 lb mole CO_2/min
1.7 lb CO_2/min

30 to 14.7 PSIA

Assume all CO_2 is vaporized.

Feed rate: 0.211 lb mole mixture/min

Overhead: 0.038 lb mole CO_2/min
1.67 lb CO_2/min

Bottoms: 0.173 lb mole MEK/min

6. Size Columns, Flash Vessels, Accumulators

800 PSIA Vessel (FVI)

Vapor rate = 9215 lbs/hr
Liquid rate = 553 lbs/hr

ρ_g = gas density = 11.1 lb/ft^3 at 800 psia and 68°F

$\emptyset = \sqrt{\rho_g/0.075}$ = 12.2

G = gas velocity, lb/hr ft^3

L = liquid velocity, lb/hr ft^3

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For ID = 14" case, cross-sectional area = 1.069 ft^2

$G = 8620$ lb/hr ft^2
$L = 518$ lb/hr ft^2

$\frac{L\emptyset}{G} = 0.73$ $\frac{G}{\emptyset} = 710$

Use generalized loading velocity correlation p. 18-23 Perry (1973) to determine that the 14" ID rates are acceptable.

HETP -- no experimental information available; use 10", six theoretical plates = 5 ft. Use 16" OD Sch. 80 pipe; Design pressure = 1000 psia; carbon steel; 6' Str. section; flanged bottom for connection to reboiler; 100% X-rayed; packing. Cost, vertical fabrication.

Installed cost = (base cost X CAF) x F_p x price index x modular factor

$= 800 \times 2.5 \times \left(\frac{273}{120}\right) \times 4.23 = \$19.2K$

300 PSIA VESSEL (FV2)

6" OD Sch. 10 carbon steel pipe x 6'; flanged; packing; 100% x-rayed.

Installed cost = cost x modular factor = 1460 x 4.23 = $6.2K

FV3

32" ID x 3' Design P = 50 PSIA

Installed cost = 800 x 4.23 = $3.4K

FV4

8" OD Sch. 40 carbon steel pipe x 4'; flanged; 100% x-rayed; design P = 1000 psia

Installed Cost = 2064 x 4.23 = $8.7K

LPA

After blowdown of CRV to 300 psia, remaining CO_2 in CRV is directed to LPA.

14.5 ft^3 CO_2 @ 300 PSIA and 60°F ÷ 0.35 ft^3/lb = 42 lb CO_2

Specific volume CO_2 at 60°F 30 psia = 4 ft^3/lb
15 psia = 6 ft^3/lb

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Have 42 lb CO_2 to be added to LPA which is at 15 psia at end of cycle; want final P to be 30 psia

$$\frac{42 + Q \text{ ft}^3 \div 6 \text{ ft}^3/\text{lb}}{20 \times 0.8 + Q \text{ ft}^3} = \frac{1}{4} \frac{\text{lb}}{\text{ft}^3}$$

$Q = 456 \text{ ft}^3$ = vessel 6' D x 16.2' L

Installed cost = 3900 x 3.18 = \$12.4K

HPA

Need to hold 5 mins x 145 $\frac{\text{lbs}}{\text{min}}$ = 725 lbs CO_2

725 lbs x $\frac{0.04}{\text{lb}}$ ft^3 (@ 1500 psi & 50°C) = 29 ft^3

Use horizontal vessel 22" ID, 24" OD x 11' L carbon steel.

Installed cost = base cost x F_p x price index x modular factor

$$= 1200 \times 4.35 \times \left(\frac{273}{120}\right) \times 3.18 = \$37.8K$$

7. Compressors

C1

9240 lb/hr

P_i = 800 psia
T_i = 18°C (64°F)
V_i = 0.09 ft^3/lb

P_o = 1500 psia

= 832 ft^3/hr @ inlet conditions

Approximate HP:

$$\frac{10 \text{ Btu/lb}}{0.65} \times 9240 \text{ lb/hr} \times 3.93 \times 10^{-4} \frac{\text{HP hr}}{\text{Btu}} = 56 \text{ HP, say } 60 \text{ HP}$$

C2

730 lb/hr

P_i = 300 psia
T_i = 21°C (70°F)
V_i = 0.38 ft^3/lb

P_o = 800 psia

= 277 ft^3/hr @ inlet conditions

Approximate HP:

$$\frac{26 \text{ Btu/lb}}{0.65} \times 730 \text{ lb/hr} \times 3.93 \times 10^{-4} \frac{\text{HP hr}}{\text{Btu}} = 12 \text{ HP}$$

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C3

300 lb/hr P_i = 14.7 psia (worst case) P_o = 300 psia
T_i = 16°C (60°F)
V_i = 9 ft^3/lb

= 2700 ft^3/hr @ inlet conditions

Approximate HP:

$$\frac{84 \text{ Btu/lb}}{0.65} \times 300 \text{ lb/hr} \times 3.93 \times 10^{-4} \frac{\text{HP hr}}{\text{Btu}} = 15 \text{ HP}$$

Compressors: oil-free reciprocating; skid mounted
C1: R1X model 2KJ1BG-15
C2: R1X model 1K1BG-6
C3: R1X model 2K2BG-70

Equipment Item	Skid Cost, $		Installed Cost, $ (000 omitted)
Compressor C1	48.0		
Compressor C2	31.2		
Compressor C3	25.4		
	104.6		
	+ 20.9	(20% Installation Factor)	
	125.5		
	+ 25.1	(20% Engineering, Indirects)	$150.6
	150.6		

8. Heat Exchangers

FV1 Exchanger

$$15.38 \frac{\text{Btu}}{\text{lb}} \times 9240 \frac{\text{lb } CO_2}{\text{hr}} = 142{,}100 \text{ Btu/hr}$$

$$A = \frac{q}{U \times LMTD}$$

LMTD $\cong$ 20°F ... based on work with similar systems

U $\cong$ 100 Btu/hr ft^2 °F

$$A = \frac{142{,}100}{2000} = 71 \text{ ft}^2\text{; say } 100 \text{ ft}^2$$

Shell and Tube in kettle reboiler; cs/cs; 1800 psi

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Cost = [Base cost (Fd + Fp) x Fm] x Price Index

$= 2000\ (1.35 + 1.1) \times 1.0] \times \left(\frac{273}{120}\right) = \$9.6K$

$(= 96\ \$/ft^2)$

Installed cost = 9.6 x 3.28 = \$31.4 K

FV2 Exchanger

$40\ \frac{Btu}{lb} \times 730\ \frac{lb}{hr} = 29{,}200$ Btu/hr

$A = \frac{q}{U \times LMTD}$

LMTD = 30^oF

U = 75 Btu/hr $ft^2\ ^oF$

$A = \frac{29{,}200}{30 \times 75} = 13\ ft^2$

use coil at $\$100/ft^2 = \$1300$

Installed cost = 1300 x 1.83 = \$2.4K

Reflux Exchanger

540 lb CO_2/hr @ 1500 psia 122^oF

Cooling water at 80^oF

$\Delta t_h = 122^oF - 110 = 12^oF$

$\Delta t_c = 85^oF - 80 = 5^oF$

CO_2 ΔH at 1500 psia from 122^oF to 85^oF = 46 Btu/lb

q = 46 x 540 = 25,000 Btu/hr

$W_{H_2O} = \frac{25{,}000\ Btu/hr}{1\ \frac{Btu}{lb\,^oF}\ (110^oF - 80^oF)} = 833$ lb/hr

= 100 gallon/hr

LMTD = 8^oF

U = 50 Btu/hr $ft^2\ ^oF$

$A = \frac{25{,}000}{8 \times 50} = 63\ ft^3$

Use double pipe exchanger

Installed cost = Base X Fm x Fp x Price Index x 1.83

$= 370 \times 1.85 \times 2.0 \times \left(\frac{273}{120}\right) \times 1.83 = \$5.7K$

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Summary of Regeneration System Costs:

	Total Equipment Cost	Modular Factor	Installed Cost
Compressors C1-C3	-	-	150.6
Carbon Regeneration CRV	24.49	4.23	103.6
Separator FV1	4.54	4.23	19.2
FV1 Heat Exchanger	9.56	3.28	31.4
Separator FV2	1.46	4.23	6.2
FV2 Heat Exchanger	1.30	1.83	2.4
Separator FV3	0.80	4.23	3.4
Separator FV4	2.06	4.23	8.7
Reflux Heat Exchanger	3.11	1.83	5.7
Accumulator HPA	11.88	3.18	37.8
Accumulator LPA	3.90	3.18	12.4
			$381.4

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APPENDIX C. MISCELLANEOUS CALCULATIONS

1. Determination of Gasoline Vapor Composition as a Function of Amount of Gasoline Removed

Initial gasoline composition from Muller, et al., (1966). K-values at 1 atm and 75°F for the 28 components identified in the SAE report were taken from the DePriester charts (e.g., from those in Smith, 1963). The liquid-mole fractions were calculated; using the K-values, the equilibrium vapor composition at 1 atm in air was determined. N-pentane was taken as the key and relative volatilities to n-pentane calculated. Using the relationship:

$$\ln \frac{W_{1F}}{W_{1I}} = \alpha(\ln \frac{W_{2F}}{W_{2I}})$$

where W_{1I} and W_{1F} are the moles of component 1 in the liquid before and after partial volatilization, respectively; liquid compositions were calculated as a function of weight of the gasoline removed. The results for the four lightest components (which had the greatest changes in composition) are shown in Table VII.1. The calculations were performed with a computer program written in APL.

2. Estimation of Concentration of Gasoline Vapor Components in Carbon Column Desorption Effluent

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Maximum possible gasoline component mole fraction: if all desorbed in one bed volume of CO_2, if molecular weight taken to be that of the lighest component, n-butane.

15.5 g of carbon in a 36.3 cm^3 column.
Carbon real density: 2.0 g/cm^3.
Carbon occupies 15.5 g/2.0 g/cm^3 = 7.8 cm^3.
CO_2 occupies 36.3-7.8 cm^3 = 28.5 cm^3.
Maximum density of CO_2 = 0.87 g/cm^3 @ 1600 psia, 25°C.
0.87 g/cm^3 x 28.5 cm^3 = 24.8 g CO_2 in column.
= 0.56 g mole CO_2 in column.

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Mass of adsorbate = 0.28 g/g carbon x 15.5 g carbon = 4.3 g adsorbate.

If all adsorbate taken to be n-butane = 0.07 g moles.

Maximum mole-fraction of hydrocarbon adsorbate = $\frac{0.07}{0.07 + 0.56} = 0.11$.

3. Vapor-Liquid Equilibrium Data for CO_2-EtOH and CO_2-MEK Systems

For initial work using the Lewis-Randall rule, vapor pressure data for EtOH and MEK were taken from "Ethyl Alcohol Handbook" (1960) and Ambrose, et al. (1975), respectively. Fugacities for pure components were taken from a generalized fugacity coefficient chart, e.g., one in Smith (1963). Critical constants and accentric factors for the Peng-Robinson equation of state were taken from Smith, (1975). The Peng-Robinson calculations were performed with a computer program written in APL.

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